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A

SYSTEM

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A

SYSTEM

OF

CHEMISTRY.

BY

J. MURRAY,

LECTURER ON CHEMISTRY, AND ON MATERIA MEDICA AND PHARMACY, EDINBURGH.

IN FOUR VOLUMES.

ROYAL ARMY MEDICAL COL
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PREFACE.

Chemistry may perhaps claim this advantage over the other branches of Physical Science, that it presents a field of inquiry almost unlimited. Its great object is to trace the combinations of matter; and when it has succeeded in discovering the composition of any substance, so far is this from closing the investigation, that it rather multiplies the subjects of research; the constituent principles of the decomposed substance, if before unknown, are submitted to new experiment; and the progress of this analysis is nearly indefinite.

At the same time, the evidence on which the doctrines of Chemistry rest, is less rigorous than that which forms the basis of the Mathematical Sciences. It does not amount to strict demonstration, but consists of a series of inductions, drawn from observation or experiment, or sometimes only inferred by analogy.

From these circumstances is derived the character which distinguishes this department of natural knowledge,—that it is eminently and rapidly progressive: its facts are daily augmented; its principles corrected or confirmed; new objects of investigation are perpetually occurring; and while its acquisitions are real, they still open farther prospects of discovery.

This character is well exemplified in the history of Chemical Philosophy. If we compare the Mathematical Sciences in their present state, with that in which they were left by Newton, though they have acquired some important truths, they exhibit no revolution, such as that which has marked the progress of Chemistry. Nor is this owing, as some perhaps might imagine, to Chemistry having become the subject of philosophic investigation at a later period; for it still continues to advance, with equal or accelerated steps. One not acquainted with its leading character, might have been disposed to conclude, on the establishment, of what has been termed the Modern Theory, by Lavoisier, that the outline was nearly completed, and that the parts only remained to be filled up. Its progress since that time,—the different aspects which various parts even of its theory have assumed,—the discovery of new agents, possessed of

the most important chemical powers,—and the views which these unfold to us, prove the fallacy of such an opinion, and how vain the attempt is to assign limits to the Science.

From the revolutions which thus more or less occur in the doctrines of Chemistry, from the rapid accumulation of its facts, and the increasing extent of its applications, arises the necessity, or at least the advantage, of frequently exhibiting a systematic view of it in all its details. Where new principles too, have been established, it is not easy to assimilate them with arrangements founded on different views, more especially where such principles have extensive and numerous relations.

If there is any feature which I may be allowed to point out, as more peculiarly belonging to the present System, it is that which may arise from the attention bestowed on the general doctrines of Chemistry. These I have reviewed, and endeavoured very amply to illustrate, convinced, that in a department of Physics so extensive, the most important object, to which the attention of those undertaking its study can be directed, is that relating to the principles by which its individual facts are connected and arranged. Without an intimate knowledge of these, the Science is not ac-

quired; and the acquisition of such a knowledge, at once facilitates and renders more interesting, the prosecution of its minute details and applications.

In the consideration of these doctrines to this extent, the principle which is always to be kept in view, in a Work designed, in some measure, for elementary instruction,—that of advancing only from what is known to what is unknown, and of not supposing the reader acquainted with facts which have not been stated, has obliged me, in several instances, to refer the discussion, on subjects more abstruse or complicated, to Notes at the end of the volume. By this arrangement, I flatter myself, that I have attained every advantage. While I have given in the text a view sufficiently ample for those beginning the study, I have been enabled, in these disquisitions, to engage more freely in the discussion of questions interesting to others, who are already advanced, and to whom a more general statement would prove less satisfactory. These notes, it will be obvious, are in a great measure independent of the text. The work would be complete as an elementary system though they were not introduced; and they are to be regarded merely as serving to turn the attention of those who have made some progress in chemical studies, to such parts of the

theory of the Science as are more doubtful and obscure. To those who are unacquainted with Chemistry, I may therefore be allowed to recommend, that, on a first perusal, no attention should be paid to these more abstruse investigations, which I have detached from the body of the Work.

On the arrangement I have adopted, I do not conceive it necessary to make any observations. It has been my object to render it simple, to place the different subjects in that order which I conceived best calculated to facilitate their study, and, without losing sight of a systematic method, to admit of those aids from analogy which the present state of Chemistry demands.

With regard to the nomenclature I have used, it can scarcely happen, in the present state of chemical language, but that some difference of opinion will exist as to the propriety of particular expressions. The modern nomenclature, in any form under which it has appeared, is not strictly systematic, but in particular cases, has admitted deviations from its general principles, to gain the advantages of conciseness, euphony, and facility of derivation and combination. As to the limits of such deviations, and the cases, even where they are admissible, a perfect coincidence of opinion cannot

yet be expected; the lapse of time only will establish uniform usage. It may be sufficient for me to say, that I have used the modern nomenclature, as translated by Dr Pearson; in general, though not invariably, with the corrections of Mr Chenevix. While I consider the language of Chemistry as indebted to the observations of this Philosopher for additional precision, he appears to me, in some cases, to have adhered too strictly to the original derivation of the terms from which compound names are formed; and, in other cases, to have too much disregarded the genius of the language to attain systematic perfection. I have followed the example of Mr Davy, and some other British chemists, in preferring the term Nitrogen, originally proposed by Chaptal, to that of Azote. While the one violates the principles on which the modern nomenclature is founded, the other is strictly conformable to them, and was rejected at the framing of that nomenclature on very frivolous grounds. I have also ventured to substitute the term Potassa for Potash or Potasse, names in themselves extremely exceptionable; the former, besides its coarseness, being used in the language of commerce to denote a different substance; the latter being a French, not an English word; and neither of them corresponding in termination with the names of the other alkalis. Chemists have indeed

been always dissatisfied with them, and they have remained in use only from the want of a better appellation.

One of the advantages, of not the least importance in a systematic work, is that of affording references to original authorities. I have been careful to insert those which I have consulted; and as the greater number of readers will have easier access to the British than to the foreign philosophical journals, I have always referred to the former, where the memoir quoted has been translated.

Edinburgh,
Nov. 1. 1806.

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— 195. — 4. — 48 — 40
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INTRODUCTION.

NATURE, OBJECTS AND APPLICATIONS OF CHEMISTRY.—GENERAL VIEW OF ITS HISTORY.—PRINCIPLES OF ARRANGEMENT.

THE phenomena which are the objects of investigation in the different branches of Physical Science, arise from the exertion of the powers with which Matter is endowed. Gravitation, under all its modifications, is the cause of those sensible motions, the study of which constitutes the different branches of Mechanical Philosophy: the attractions of Magnetism and of Electricity, produce classes of phenomena which it belongs to these sciences to investigate; and from the exertion of two powers, those of Heat and Contiguous Attraction, arise the actions which are arranged under the Science of CHEMISTRY.

Contiguous Attraction is that force exerted between the minute particles of matter, when they are placed in apparent contact; which unites them together; and, when these particles are of different kinds, forms substances distinguished by the possession of new properties. It is exerted by every body towards a num-

ber of others; to each with a different degree of force; whence arises an extensive series of combinations, which constitute an important part of the economy of nature, and which are often capable of being regulated by artificial arrangement.

This force is always modified in its action, by the power of Heat or Repulsion, the tendency of which is to separate the particles of bodies from each other, and which thus, according to circumstances, counteracts or favours the exertion of contiguous attraction. All cases of chemical action are the results of the united or the predominant operation of these powers.

The actions which it is the object of Chemistry to investigate, are thus uniformly exerted between the minute particles of matter; and this constitutes a leading distinction between it and the other branches of physical science, the investigations of these being directed to actions exerted between masses of matter always sufficiently sensible, and often of immense size.

From this arises another distinction, between Chemical, and what may be denominated in opposition to it, Mechanical action. The former, incapable of being exerted at any sensible distance, takes place only when the particles susceptible of it are brought into apparent contact; while the latter may be exerted between masses of matter at great distances; and in all cases, its action is perceived only at the surfaces of bodies. Hence the motions to which it gives rise are capable of being measured with accuracy, as to their direction and force, and the sciences which investigate them can be established on mathematical evidence.

The actions of chemistry are more obscure and instantaneous; taking place only at the point of contact, they admit of no precise calculation as to their intensity; and are discoverable almost solely from changes in the constitution of the bodies between which they have been exerted.

In the last place, chemical action, by uniting the particles of matter, changes their existing arrangement; subverts the properties of bodies, and produces others with qualities more or less different. It is a striking character of chemical action, thus to give origin to substances having new properties; and it may justly be regarded as the great source of the various qualities with which bodies are endowed. From any other species of physical action no change of this kind results. The effect is merely to excite or communicate motion, or to modify it in masses of matter, whence no alteration in their intimate constitution can be produced.

The different objects of these two departments of physical science might easily be illustrated by the slightest survey of the different points of view under which the same substances are studied by the Mechanical and Chemical Philosopher. The one, for example, in subjecting Light to his examination, considers it merely as a substance of great tenuity, moving with velocity in right lines, and capable of having its motion stopt, or its direction changed by the action of other bodies upon it, giving rise, by these actions, to the phenomena of optics. The other, without attending much to the phenomena which the motion of

light under different modifications presents, traces it in its more intimate actions on bodies, as it exerts attractions to their particles, occasioning separations and decompositions, and thus producing total changes of properties; effects arising, not from the motion of the entire ray of light, but from intimate and permanent combinations of its particles with the particles of the bodies which it has thus changed. To the Mechanical Philosopher, Air is a subject of attention merely as a mass possessing mobility, elasticity, and weight. The Chemist, on the other hand, subjects it to his experiments, with the view of discovering whether it is simple or compound; and, instead of regarding it, with the mechanical philosopher, as a homogeneous fluid, he finds it to be composed of various ingredients, which are capable of producing very different changes in bodies with which they combine: he traces these combinations, and discovers the agency of its principles in exciting combustion, in promoting vegetation, and in supporting animal life. Water, in a system of Mechanical Philosophy, is a subject of attention only in so far as it is susceptible of motion, and affects bodies by its impulse or gravity. But in Chemistry, its numerous combinations are investigated; its elements are discovered; and the operation of these elements, as they are disengaged by the decompositions it suffers, is traced, not only in mere chemical processes, but on a scale of greater magnitude, in some of the most important operations of nature. Lastly, Solid substances are regarded by the Mechanical Philosopher only as they are endowed with

figure, hardness, or cohesion, or as presented to him in various states of motion. But, from the Chemist, they claim a more minute examination, as to the actions which the particles of each exert towards those of others, and the combinations into which they thus enter.

By these characters, Chemistry may be sufficiently distinguished from the other departments of natural knowledge; and, in conformity to these views, may be defined, The science which investigates those actions which are exerted between the minute particles of matter, by which the properties of bodies are altered, in consequence of their transition into new combinations or new forms.

From the exertion of contiguous attraction between the particles of the same kind of matter, modified by heat, arise the various forms in which bodies exist; and from its exertion between particles of different kinds, are derived the greater number of substances which compose our globe. A body may be presented to us apparently homogeneous, but which chemical research shall discover to consist of dissimilar parts, or of particles having different properties; and when we examine the various substances existing in nature, we find them to be in general compounds of this kind. We are able, also, by combining different kinds of matter together, to form substances which nature has not produced. The objects of chemistry are to trace these combinations, and to discover all their results, to observe the phenomena by which they are accom-

panied, and determine the laws by which they are regulated.

From such investigations arise numerous applications to purposes of practical utility, or to the elucidation of natural phenomena; many of the changes which occur in nature arising from the chemical actions of various substances on each other, and many of the arts being nothing more than a series of chemical processes. These applications, in all their extent, it would not be possible to trace within the limits of an introductory discourse. A general sketch only can be presented.

The ATMOSPHERE, or that mass of elastic fluid which surrounds the globe, is, by its chemical powers, an important agent in the processes of Nature. It serves, for example, to equalize the distribution of heat over the surface of the earth. Expanding, and of course becoming specifically lighter from increase of temperature, a current of air always ascends from any part of the earth's surface that is much exposed to the solar rays; it carries off the excess of heat, which would otherwise accumulate, while its place is supplied by colder air, which is pressed in from every side. The warmer air is wafted to colder regions, and parts, in its progress, with the heat it had received. A circulation is thus established, by which the extremes of heat and cold, that would otherwise have rendered the greater part of the globe uninhabitable, are prevented; while, by these motions of the mass of air, its purity, as adapted to the support of animals, is more effectually preserved. Nor does the atmosphere

merely convey heat, and equalize its distribution; it contains an immense quantity of the same power in a concealed state, which, by many chemical combinations, is rendered sensible,—which is the source of the heat produced by the burning of combustible matter, and of that which animals generate, preserving them constantly warmer than the surrounding medium. It is not less useful as the agent by which the circulation of Water is established. Assisted by heat, it is capable of elevating a portion of this fluid in vapour; which, cooled in the higher regions, or in colder climates, descends in the form of dew, rain, or snow; and, by the declivity of the land, is conveyed over its surface, and returns to the sea. Lastly, air is indispensable to the support of vegetables, and the existence of animals. To plants, it affords a considerable part of their nourishment. To animals it is still more necessary, its abstraction for a few minutes causing death. And in both, its agency is chemical: it suffers changes of composition, and produces reciprocal changes in the animal and vegetable systems.

Water is the medium of various important chemical changes in nature. Like air, it operates in equalizing temperature, partly by its motion, and partly by its changes of form: in passing to the state of ice it evolves heat, and absorbs it when it returns to that of water, and by both moderates the transition of seasons. It acts upon the solid parts of the earth's surface, and causes their disintegration; and in supporting animals and vegetables, it undergoes decom-

position, and furnishes principles which contribute to the formation of their products.

The operations of the MINERAL KINGDOM are more concealed from us; but we can have no doubt of their dependance on chemical principles, and we indeed perceive them occasionally exemplified. The greater part of the substances which compose the crust of the earth are compounds, and have of course been formed by chemical combinations; and the sublime, though obscure speculations of Geology, are founded on the conclusion which facts sufficiently establish, that affinities have at one time been exerted between these substances, or between their principles, while existing in the fluid form.

Nor is chemical influence less conspicuous in the ANIMATED WORLD. The substances which are received into the animal and vegetable systems, and which are necessary for their support and growth, suffer decomposition, and their principles are combined in new modes and proportions in the vessels of the organic being, forming its substance and various products. Although the process may be modified by the circumstances under which it takes place, it is still essentially chemical; and chemistry is capable of elucidating some of the most important subjects of investigation in animal and vegetable physiology. In Vegetation, we perceive a series of changes, the result in a great measure of chemical affinities. From the moment of its commencement, air and water are absorbed, are decomposed, and their principles combined in the vessels of the plant; and from these com-

binations, the numerous and diversified products of vegetables are formed. If other agents are necessary, or subservient to the process, it is still by their chemical agency. Light, by the affinities it exerts, aids the decomposition of the water which the plant absorbs; and manures accelerate the process, and improve its products, by furnishing, in a less combined state, and in larger quantity, the same principles which air and water supply. In the series of changes which are carried on in the Animal System, the influence of chemistry is equally to be traced. In examining the process of digestion, it discovers the chemical quality of the gastric fluid, by which it is fitted to dissolve the food. In investigating the function of respiration, it unfolds the nature of the chemical changes which the blood suffers in the lungs; the evolution of a principle, which, if retained, might prove hurtful, and the absorption of that part of the air which is immediately necessary to life. In the same process, it discovers the source of animal heat, or of that power by which animals are enabled to preserve themselves uniformly at a temperature superior to that of the medium around them. In perspiration, it discovers a function subservient to respiration, and fulfilling nearly the same purpose. And in secretion, it traces the various chemical products formed from a common fluid by the exertion of complicated affinities. Lastly, by analysing the fluids and solids of the animal body, it throws light on the researches of the physiologist, and guides, even in some cases, the practical inquiries of the physician.

But Chemistry is not to be valued merely from its connexions with the phenomena of nature. Its importance is not less conspicuous in its relations to the Arts. Strictly speaking, the greater number of the arts have preceded the cultivation of any science; they have originated from the necessities of man at an earlier period, and have often been improved by accident, or by the mere routine of practice. Still, their principles are dependent on science; and although scientific men labour under disadvantages in such researches, from the jealousy of artists, and the want of practical experience; from them, in modern times at least, have originated some of the most important improvements the arts have received.

Agriculture, the most important of the arts, and that which is perhaps most susceptible of indefinite improvement, is more directly connected with chemistry than with any other science. Vegetation is little else than a chemical process, or it consists of a series of changes of composition, terminating in the formation of certain products. It must be admitted, that the causes by which these changes are effected are not altogether under our controul; but neither are they wholly exempt from it. By certain arrangements of circumstances, hitherto, indeed, in a great measure empirical, we can accelerate the process, and even increase the quantity of product, or to a certain extent change its nature. It is perhaps not being too sanguine to hope, that our power in these respects will be farther extended, as our knowledge of the chemistry of vegetation is advanced. We al-

ready know something of the influence of soil, and of the action of manures; and it is not unreasonable to indulge the expectation, that chemistry may still unfold to us more skilful modes of applying the agents on which the nutrition of vegetables depends, or of regulating those circumstances which influence the formation of their various products.

In the treatment of the products of vegetation, we often find chemical agency exemplified. In bleaching, by the application of a process purely chemical, we change the colouring matter of the thread, and render it capable of being easily removed. In dyeing, we extract the colours of many substances by solution, heighten their brilliancy by the admixture of chemical agents, and, by the intervention of others, fix and render them permanent in the cloth. In fermenting, by a proper regulation of circumstances, we change the principles of the fermenting substance, and form a very different product, wine, or fermented liquor: And, by distillation, we separate from these the ardent spirit, in which their principal qualities reside. The art of the chemist is not less strikingly displayed in the processes for extracting and refining sugar, preparing starch, indigo, &c. in the fabrication of paper, and in the preparation of many other useful products obtained from the vegetable kingdom. The principles of all these arts have been established by the researches of modern chemistry; and in the greater number of them, their manipulations have been improved by the application of scientific skill.

In the treatment of animal substances, other appli-

cations of chemistry may be pointed out. Tanning, the manufacture of soap, glue, and a number of others, are mere chemical processes, the theories of which have been successfully elucidated.

The mineral kingdom affords a number of substances, which, to be adapted to the uses of man, must undergo many operations of art; and these are in general of a chemical nature. The extracting and working of metals, arts so important to civilized society, and the effects of which, in all their extent, it would be difficult to appreciate, are mere branches of practical chemistry. The production of glass, the most beautiful and one of the most useful gifts of art to man, is the result of a simple chemical combination. From variations in the process, and additions of certain ingredients, arise the arts of enamelling and imitating the gems. And the processes employed in the fabrication of pottery and porcelain, depend on similar combinations, regulated entirely by this science.

Not only is chemistry of advantage, from its relations to the arts; it is also interesting and valuable from the connexions it has with many of the practices of common life. Illustrations of this kind might be derived from the knowledge it conveys, by the discovery of the laws of heat. The peculiar effects arising from the action of this power upon matter, the sensations it excites, the modes in which it is conveyed through bodies, and its evolution and absorption, constitute phenomena familiar in their occurrence, the scientific knowledge of which is in the highest degree interesting, and which admit of the most nu-

merous and important applications. From the multiplicity of its objects, and extent of its relations, no science, indeed, can be more interesting to the speculative inquirer, or can promise more practical advantage; there is none of which the progress in modern times has been so rapid, or of which the prospect of improvement is more unlimited.

In surveying the progress of chemistry, we find the earlier part of its history involved in obscurity and fable. We are able only to discover traces of the practice of certain arts from the most remote antiquity, the principles of which are chemical. But this undoubtedly affords no reason to conclude, that they originated from any previous acquisition of chemical science. They must have been the result of casual observation, or of experiments dictated by necessity, and they were long taught and practised without any knowledge of the principles on which they are founded.

Of these arts, metallurgy, or the art of extracting metals from substances with which they are naturally mixed, of purifying, casting and forging them, was probably of earliest invention, since some knowledge of it must have been indispensable in that state of society in which the others would be cultivated. Gold, silver and copper, metals which are found native, and which are easily worked, appear, from ancient history, to have been first applied to use. Iron, which is much more refractory, was of later introduction. The properties and uses of these, as well as of lead and tin, were, however, known at a very early period, nor

have we any records of their discovery. Other chemical arts, as that of making brick, and such kinds of earthen-ware as might be used in the preparation of food, those of fermenting, of bleaching, dyeing, and several others, though probably of later origin, were yet practised in the earliest ages.

In Egypt, particularly, the various chemical arts seem to have made considerable progress, and that country has been celebrated as the parent of chemistry. Its history among the Egyptians, is, however, nothing but the history of the progress of the arts among a civilized and luxurious people. Their practice might be gradually improved, and new facts occasionally brought to light; but their principles were not discovered; no relation was traced among them, nor was it known that they were parts of a common science.

Chemistry formed no part of the Grecian philosophy. A number of observations respecting the chemical properties of bodies may be found in the writings of THEOPHRASTUS, ARISTOTLE, and others. But these were scattered and altogether unconnected. Nor are the vain and hypothetical speculations of the schools on the elements of matter, the nature of fire, air, water and earth, the figures of the particles of bodies, and their modes of action, entitled to the appellation of chemical philosophy. Such as they were, they rather bore a relation to general physics.

Can any cause be assigned for this slow progress, or rather this late origin, of Chemistry? While it remained thus uncultivated, other sciences were con-

siderably advanced. Astronomy had been studied with success. Arithmetic, with the first principles of Geometry, were early known: and these, with some other branches of physics, were advanced by the labours of the Grecian philosophers.

It may in part be ascribed to the peculiar nature of this science. Its most powerful agents, and those most extensive in their operation, are substances with which we are not familiar, and which are even not easily recognized, and the actions which it investigates being exerted between the minute particles of matter, its phenomena are complicated and obscure, while the connexions between them, and the actions by which they are produced, are remote and not easily traced. The difficulty, therefore, of observing accurately the phenomena, and of discovering their causes, must have retarded the progress or rather the rise of the science. With this, another cause concurred. Chemical investigations can be prosecuted successfully only by experiment; and this method of interrogating Nature, or at least its importance, was unknown in the ancient world. Arithmetic and geometry require for their cultivation only pure intellectual exertion; and astronomy, as it existed among the ancients, depended, for its advancement, principally on patient observation. These might, therefore, be successfully cultivated, while Chemistry, which is so immediately dependent on experiment, would, as a science, remain unknown. The delusions of Alchemy gave rise to the experimental method of investigation, and thus not only laid the foundation of chemical science, but

perhaps contributed more than any other event to the superiority of the modern over the ancient mode of philosophizing.

To Alchemy, Chemistry undoubtedly owes its origin. As a distinct branch of knowledge it had no existence, prior to the period when the pursuit of the alchemists commenced. The chemical properties of bodies had seldom been made the subject of investigation, and the gradual improvement and extension of the chemical arts were rather the result of chance, than of direct inquiry suggested by any principle. By the multiplied and laborious experiments of the alchemists, some knowledge of these properties was attained, and gradually enlarged; an apparatus was invented; rules were delivered for conducting chemical processes; and many of the principal agents of chemistry were discovered, arranged under classes, and characterized by their most striking properties. The knowledge thus slowly acquired, was indeed for a time directed to a chimerical pursuit; but the value of the acquisition was not diminished, while the foundation was laid of more rational and successful investigations. "Alchemy" says Lord Bacon quaintly, though with much justness, "may be compared "to the husbandman, of whom Æsop makes the "fable, that when he died, told his sons that he had "left unto them gold buried under ground in his "vineyard; and they digged over all the ground, and "gold they found none; but, by reason of their stir-"ring and digging the mould about the roots of their "vines, they had a great vintage the year following;

"so, assuredly, the search and stir to make gold hath "brought to light a great number of good and fruit-"ful inventions and experiments *."

It has been found difficult to fix with precision the date of the rise of Alchemy, and we know nothing of the circumstances from which this singular delusion originated. The art of transmutation is mentioned before the close of the fourth century; and during the sixth and seventh centuries, a number of treatises were written on it in the Greek language, scarcely intelligible, however, from their obscure and enigmatical style. In the seventh century it was communicated to the Arabians, and with them originated a new pursuit, which was soon incorporated with the search after gold. The same agent, it was supposed, which was the object of discovery as capable of converting the baser metals into silver and gold, would, by its operation on the animal system, prevent or remove disease and confer immortality. This notion was fondly adopted, and ever after we find it conjoined with the original object of Alchemy.

Amid the darkness of the middle ages, these delusive labours continued to be prosecuted with increased ardour; and it is probably during this period, extending from the eleventh to the sixteenth century, that the greatest number of real chemical discoveries were made. In the thirteenth century flourished Roger Bacon, to whom gunpowder and phosphorus seem to

* Bacon's Works, 4to, vol. i. p. 18.

have been known, and whose views in chemistry were greatly superior to those of his successors at a much later period. He was followed by ARNOLDUS DE VILLA NOVA, RAYMOND LULLY, ISAAC and JOHN ISAAC HOLLANDUS, and BASIL VALENTINE, of whose history so little is known, that it is doubtful whether some of the names are not fictitious, nor is it easy to assign, with precision, the discoveries they made. Those they have announced, are probably, indeed, rather the results of the continued labours of the sect, than of their individual exertions. Some of them are important. Two of the alkalies, a number of the acids, and of the neutral salts, were now known; several of the semi-metals, as they have been termed, were distinguished from the metals hitherto in use; many metallic preparations were introduced; the instruments of chemical analysis, and the methods of conducting chemical operations had received material improvements; and the chemical arts had slowly advanced to greater perfection.

PARACELSUS and VAN HELMONT close the list of distinguished alchemists. The former, one of the most singular characters that the history of chemistry presents to our observation, first shook the blind and implicit acquiescence of physicians in the doctrines of the ancients, and contributed to introduce modes of thinking more favourable to the progress of science. By having introduced a number of metallic preparations into medical practice, and in some measure established their success, he laid the foundation of chemical pharmacy, and the attention of those who

prosecuted these researches was thus in part withdrawn from the fruitless pursuit after the art of transmutation, and directed to an object beneficial in itself, and unconnected with concealment and imposture. To Van Helmont, with all his extravagance, scientific chemistry is probably more indebted than to any of the alchemists; his inquiries were in general directed to more useful objects, and conducted, perhaps, with more just views. He investigated with considerable success the properties of several of the aërial fluids produced in chemical operations; and although his researches were not immediately prosecuted, they were never wholly forgotten, and it is easy to trace them in the subsequent experiments of BOYLE and HALES.

From this period alchemy rapidly declined. The experience of many centuries had sufficiently proved the fallacy of the hopes which the alchemists had entertained, while so many instances of fraud and imposture had been detected, that little credit was given to their pretensions, and a belief of the total futility of the art began to be entertained.

At the same time commenced that revolution in philosophy, so favourable to the progress of true science. The scholastic system, that singular combination of subtilty and absurdity, began to decline, and a philosophy more rational in its principles and more useful in its objects, arose from its ruins. Chemistry participated in this revolution; and from this period may be dated its progress as a science. Bacon first assigned it this rank, and gave it, in his survey

of human knowledge, its peculiar characters: he reviewed its history, exposed the errors of its professors, and suggested a number of investigations which he supposed might be successfully prosecuted.

The institution of the different learned societies in Europe aided the progress of Chemistry in common with the other experimental sciences. In their early memoirs, we find many chemical disquisitions; and Chemistry long continued the principal object of their researches. Many of its processes were improved; facts were multiplied; applications traced; and a constant accession made to the stock of knowledge. KUNCKEL, HOMBERG, the LEMERYS and GEOFFROYS distinguished themselves in these labours. BOYLE is justly celebrated for the extent and importance of his researches, particularly in Pneumatic Chemistry; and in the same department, HOOKE and MAYOW so far exceeded the knowledge of their times, that their discoveries were not duly appreciated, and had no influence on the pursuits of their cotemporaries, but were allowed to fall into oblivion, to be noticed in a succeeding age with admiration, as anticipations of some of the most important truths which the combined efforts of modern chemists have established.

Chemistry is indebted to NEWTON for the generalization of its phenomena, or the discovery of the principle on which its operations depend, and the observation of some of the laws by which it is regulated. In the thirty-first query, at the end of his Treatise on Optics, he states a number of cases of chemical

combination and decomposition. Some bodies, he observes, have a tendency to combine together; others refuse to unite; and each has a tendency to combine more strongly with some than with others. These phenomena he refers to a species of attraction exerted between the minute particles of matter, different in its laws from that attraction by which their masses are made to approach. The relative forces of the different attractions were afterwards investigated, and an important benefit conferred on chemistry by their being reduced to the form of a Table, by Geoffroy.

Hitherto Chemistry might be regarded as nearly a collection of insulated facts, no theory which embraced many of its phenomena having been proposed. Beccher, a German chemist, had indeed advanced some speculations respecting the elements of bodies; but these, entirely hypothetical and vague, deserve no attention, except as having given rise to the celebrated hypothesis of Stahl, which, for a considerable period, was implicitly received, and had an important influence on the progress of the science.

Of the general operations belonging to Chemistry, Combustion or Burning, is undoubtedly the most important. It is so, not merely from the striking phenomena it exhibits, and from a number of bodies being susceptible of it, but also from being the source of some of the most active chemical agents, particularly the class of acids. What still farther extends its influence, is, that the same changes are produced by some other processes, with which combustion

is therefore in some measure identified; and hence any theory of this process must be related more or less directly to a great number of chemical facts.

The explanation which Stahl gave of combustion and the changes connected with it, was extremely simple. He adopted an idea of Beccher, or rather indeed the popular idea, that combustible or inflammable bodies contain a common principle to which their inflammability is owing; this principle he named Pure Fire or Phlogiston. Combustion he conceived to be merely its disengagement under the form of the heat and light which attend the process. By its evolution, the combustible body of course loses its inflammability, and is changed in its other qualities. This inflammability, however, it was known to the chemists, could be restored to this residual substance, by heating it with another inflammable body, a change ascribed by Stahl to the transfer of the phlogiston from the one to the other. It was also known, that inflammable substances might be deprived of their inflammability, not only by burning, but likewise by the chemical action of other substances upon them. These were supposed to attract its phlogiston, and thus to produce the change.

Though no proof was given of the truth of this hypothesis, it seemed to explain so satisfactorily the phenomena of combustion, and connected together such a number of facts, that, for a considerable period, it was adopted by every philosophic chemist; and the implicit faith which was given to it conveys an useful lesson of the caution with which a theoretical system

ought to be received. "Very different from those "systems which are produced by imagination, with- "out truth, and which experience destroys, the theory "of Stahl," says the justly celebrated MACQUER, "is the surest guide that we can take for our conduct "in chemical researches; and the numerous experi- "ments which are every day made, far from invali- "dating it, become new proofs for its confirmation." It was relinquished with reluctance even when proved to be founded on a very imperfect knowledge of the changes produced in combustion, and to involve conclusions directly contrary to fact.

Chemistry continued to make a silent progress, unmarked by any splendid discovery, until Dr BLACK began the investigation of what peculiarly distinguishes the science in its modern form. The production and properties of the aërial fluids, had not altogether escaped the notice of preceding chemists. They had even been lately made the subject of experiment by HALES; yet little was really known respecting them. The distinctions between the different species of airs or gases were very imperfectly established, and the opinion of Boyle and Hales that they are only atmospheric air, modified by the processes by which they are obtained, seems to have been generally received. Respecting their origin, also, their mode of existence in different substances, or their chemical qualities, chemists had nothing but vague opinions, nor had they ever perceived the important influence of these agents in chemical combinations. Dr Black, by his discovery of Carbonic Acid, or what he named Fixed

Air, and by tracing its combinations, first communicated precise ideas on this subject; and by his still more profound discovery of Latent Heat, threw light on the formation of aërial substances, and on the most striking phenomena which attend their combinations. He thus directed the attention of chemists to Pneumatic Chemistry; and the future history of the science is little more than a detail of the discoveries which were made in this department, and the applications to which they led.

The subject was soon prosecuted by Mr CAVENDISH, by whom were discovered the existence and properties of another aërial fluid, Hydrogen; and, at a later period, the composition of Water and of Nitric Acid. Dr PRIESTLEY'S labours were still more extensive, and his discoveries in this field more numerous. To him we are indebted for our knowledge of Nitrous Gas; of the existence of Ammonia, and of several of the acids, in the aërial form: he is the discoverer of Oxygen Gas, the peculiar qualities of which, and particularly its superior power of supporting combustion and respiration, he ascertained; and he first observed the influence of Vegetation on air, vitiated by either of these processes. SCHEELE, a Swedish chemist, participates in the honour of the discovery of oxygen, as Dr Priestley's researches were entirely unknown to him. He observed, also, the properties of Azote; and demonstrated, by a variety of experiments, that Atmospheric Air is a compound of these two elastic fluids. The French chemists soon engaged in similar investigations; and

LAVOISIER, prosecuting the experiments of Black, Priestley, and Cavendish, was at length enabled to effect the most important revolution that had yet taken place in chemical science.

Although the theory of Stahl had been implicitly received, some facts unfavourable to it had long been observed, particularly, that in certain cases of combustion, the combustible body, instead of diminishing, increases in weight; and it had always been deficient in not explaining what had been long known, that the presence of air is indispensable to combustion. The discoveries in Pneumatic Chemistry placed its deficiencies still more clearly in view, and established facts absolutely irreconcilable with its principles. It was proved with more accuracy, that the presence of the air is requisite to combustion; that part of it,—the oxygen it contains, is always consumed; and that the combustible body increases in weight, not merely in the few cases which had formerly been observed, but in every case: it was even proved by Lavoisier, by accurate experiments, that the increase in weight is exactly equivalent to the weight of the quantity of oxygen which disappears: and, lastly, it was shewn, that, from the product of the combustion, oxygen could be obtained, sometimes in a pure state, by the application of heat; in other cases combined with a third body, by the intervention of a superior affinity.

From these discoveries Lavoisier drew the conclusion, that combustion is merely the combination of oxygen with the combustible body. Indebted to

Dr Black's doctrine of latent heat for the facts, that bodies in the aëriform state contain more of that principle than when they exist in the fluid or solid form, and that, in passing to these forms, they render much heat sensible, he further concluded, that the heat in combustion does not proceed from the combustible body, but from the oxygen gas with which it combines, and which contains comparatively so much more of this power. Perceiving, at the same time, no evidence for the first principle of the Stahlian doctrine, that there exists a common principle in inflammable bodies, and that there is even no necessity for supposing such a principle to explain the phenomena of combustion, he rejected it as an unfounded hypothesis. Nor was his theory confined to the process of burning. The phenomena of Deflagration and Detonation, the changes which metals suffer when heated in contact with the air, their solutions in acids, and the action of acids on inflammable bodies, were explained on the same principle; and these explanations combined, formed a general system, which included an immense number of chemical phenomena.

The new theory, seducing by its simplicity, by the satisfactory explanations it gave of so many phenomena, and by the apparent accuracy of the experiments by which it was supported, soon ranked among its defenders some of the ablest chemists of the age. It was not to be expected, however, that the established system would at once be deserted; and accordingly, though in its original state it was no longer tenable, different modifications of it were proposed, to recon-

cile it with the modern discoveries. These were defended for a time with ability and vigour, but ultimately without success: the progress of discovery aided the modern system, and the followers of Stahl at length relinquished the contest. The history of science perhaps scarcely affords an example in which a system that had long been implicitly received, was so soon overthrown: "And in the annals of the hu-"man mind, it will be difficult to find a period more "honourable to it than that which established unani-"mity so quickly on a theory which had predomi-"nated like that of Phlogiston."

So many discoveries having been made in Chemistry within a short period, and so many errors having been exploded, a change in the language was inevitable. New ideas were to be expressed, and the phraseology of old opinions, proved to be false, was to be corrected. A nomenclature was therefore proposed by the French chemists, which, although undoubtedly liable in several of its parts to objection, is founded on just principles, and has received the sanction of general usage.

Chemistry has, since this period, continued to make a rapid progress; so numerous and important, indeed, are the discoveries that have been made, that it would be an unnecessary anticipation to notice them in this general sketch. It is now so far advanced, as undoubtedly to admit of a scientific arrangement. It is not a mere collection of facts, the relations between which are imperfectly traced, but a science, or body of knowledge capable of being arranged under gene-

ral principles. The last object in this introductory discourse, is to point out the principles on which its systematic arrangement may be attempted.

The great object of Chemistry is to trace the various combinations of Matter. These take place between bodies, in consequence of the exertion of an attraction between their minute parts, or rather the phenomena of these combinations and the laws which they appear to observe are generalized, and referred to such a power. The arrangement, therefore, which the very nature of the science appears to demand, more especially with the view of communicating a knowledge of its elements, is to state the General Laws by which its combinations are regulated, and then to trace the Particular Combinations which take place between individual substances, which constitute the details of Chemistry.

Several authors have been adverse to this plan, and have urged the objection, that it is impossible to illustrate the general principles of chemical attraction but from combinations of particular substances; and as these ought not to be supposed known, they require to be previously described. It is not recollected that this is a difficulty to a certain extent unavoidable, whatever method be followed, and that it is equally impossible to give the chemical history of a single substance without supposing the learner acquainted with the general phenomena and laws of combination, or without anticipating what, according to the plan, is reserved for discussion. It will be found not difficult to follow the more natural method with advan-

tage to the learner; to illustrate the laws of chemical attraction by examples from substances familiarly known, or which, though unknown, may still be equally adapted to convey illustrations of general truths; and such truths being established, they may be farther developed in the history of the different chemical agents, while that history is thus rendered more interesting and more complete. "Whatever "science be the object of study," says VAUQUELIN, "in order that a sure and rapid progress be made in "it, it is always necessary to explain first the general "principles under which individual facts are arranged, "and which are applicable to all its operations *."

If we regard Heat as a general power, the cause of Repulsion, the nature of which is unknown, it ought, in a systematic arrangement, to follow its antagonist power Attraction. If, on the contrary, it be regarded as a peculiar kind of matter, the principles of classification require that it should be placed with other individual substances, with those to which it has the closest analogy. The latter conclusion, that which admits its materiality, seems to be established, or at least rendered extremely probable, by modern discoveries. At the same time, its action on matter is peculiar, and not capable of being brought under the laws of chemical attraction. Its chemical history, therefore, will be best placed, according to either view, after that of Chemical Attraction; and this arrangement is rendered still more necessary from the

* *Journal de l'Ecole Polytechnique*, tom. i. p. 145.

universality of the action of this power. It is contained in all bodies, and produces in them changes of importance; these require to be fully stated under the history of each; and this renders obvious the propriety, in a work designed for elementary instruction, of first stating the general effects which arise from the operation of this power, and the laws it observes. From this there is an easy transition to the history of Light and Electricity, which are intimately connected with it, and the particular combinations of which are likewise incapable of being traced.

The remaining part of the science is the chemical history of individual substances; and, with regard to this the principle which regulates chemical researches suggests the arrangement which ought to be followed.

It is the object of Chemistry to trace the combinations of matter. In doing so, it takes substances such as they are presented to us by nature, and endeavours to discover the principles of which they are composed: it separates them into their constituent parts, and observes the properties which these possess, and the chemical agencies they are capable of exerting. In these researches, it necessarily happens, that, in the series of decompositions, substances are arrived at, beyond which the analysis cannot be carried, or which we are incapable of resolving into others. These are regarded as simple, or as the elements of which others are composed. In a chemical arrangement, designed to convey a knowledge of the science, this analytic mode, by which its principles have been established, cannot be followed with advantage. It

is necessary to pursue the synthetic method, or those substances regarded as Simple are first described. They may be arranged under orders, according to the analogies which exist among them; and after their history, the Compounds they form become objects of consideration.

I consider it unnecessary to enter into the details of the arrangement I have formed on these principles. The subordinate divisions of chemical agents being founded on certain analogies more or less strict, and requiring sometimes to be modified, from the imperfections of a science so eminently progressive as Chemistry is, there is ample room for a diversity of method, both in the formation of these divisions and in the order in which they may be placed. I have adopted that which appears to me to be most simple and natural, and to secure the advantages on which the excellence of any chemical arrangement depends, —associating those substances between which there is the greatest analogy, and rendering the history of each substance, as far as possible, complete in itself, instead of being broken and dispersed.

Under these details may be also introduced the principal applications of the science, whether to the explanation of the phenomena of nature, or to purposes of practical utility.

SYSTEM

OF

CHEMISTRY.

BOOK I.

OF ATTRACTION.

ALL the phenomena of chemistry arise from the attractions and repulsions exerted between the particles of matter. The statement of the effects arising from these forces, and of the laws according to which they operate, forms the general theory of the science, and properly precedes its particular details.

The term Attraction is employed to denote the power or force by which bodies have a tendency to approach to each other, to enter into more or less intimate contact or union, and to remain in that state. Different species of this force have been observed, which, whether they be ultimately the same or not, give rise to very different phenomena, and operate according to different laws,—which must therefore be distinguished from each other.

A general distinction may be stated between them,

according as they operate at greater or less distances, and according as they affect the masses or the particles of matter.

Gravitation, the most general in its agency of any of these attractive powers, is exerted between the largest masses of matter, placed at sensible, and often at immense distances; its tendency is to cause them to approach until their surfaces are in contact, its force being directly as the mass or quantity of matter, and inversely as the square of the distance. Operating according to this simple law, its effects can be subjected to precise calculation, and of course can be predicted independent of observation.

But there are other varieties of attraction, in the action of which this law cannot be observed; which do not affect masses of matter, but are exerted only between its minute particles; which operate at no sensible distances, but only when these particles are placed in apparent contact; and which, between different substances, under apparently the same circumstances, are exerted with different degrees of force.

Of this Contiguous Attraction, two varieties can be distinctly marked; one denominated the Attraction of Cohesion or Aggregation; the other, Chemical Attraction or Affinity. The former is exerted only between the particles of the *same* kind of matter. It unites them so as to form a mass or aggregate, the hardness or solidity of which is proportioned to the force with which it is exerted; but the essential properties of the mass are always the same with those of the particles which compose it. Chemical attraction, on the

contrary, is necessarily exerted between the particles of *different* kinds of matter; and when it unites them, forms substances having qualities which differ more or less from those of the bodies which have been combined.

While gravitation is the source of all the sensible motions of the universe, contiguous attraction gives origin to many important phenomena, arising from the insensible motions of the particles of matter. Exerted between bodies of the same kind, it is the cause of the different forms in which they exist, and the regular figures which many of them are capable of assuming. Exerted between particles of different kinds, it is the source of all the combinations of matter which constitute so important a part of the economy of nature.

The question has frequently been proposed, whether the various attractions exerted by bodies depend on one general cause, modified in the varieties under which it appears, by external circumstances, or whether there are different species of attraction originally distinct from each other?

It is no doubt true, that distant and contiguous attractions observe different laws. The force of the one is in the direct ratio of the quantity of matter, and in the inverse ratio of the square of the distance. But in contiguous attraction, though the force may vary with the mass or quantity of matter, we are not only unable to demonstrate that the general law is followed with regard to the distance; there are even facts, particularly those which relate to the adhesion of bo-

dies, which have been supposed to prove that it follows a higher ratio, or is governed by a different law.

Buffon conceived the idea, which many philosophers have been disposed to receive as just, that the apparent difference between distant and contiguous attraction is owing merely to the modification arising from figure *. On the attractions of large bodies, placed at vast distances, the figures of the masses can have no perceptible influence, while, in contiguous attraction, exerted at insensible distances, the figure, as altering the relative distance materially, must necessarily operate. The varieties in the figures, then, of the constituent particles of bodies, and it may be added, also, in their magnitudes, may modify the effects of contiguous attraction, so far, that, supposing it subject to the same law as gravitation, or to be merely that power, it may still present to us results which cannot easily be subjected to calculation.

Bergman adopted this view, and Macquer, perhaps, added to its probability, by the observation †, that "if gravitation be an essential property of matter, as "there is much reason to believe, its effects cannot be "confined to very large bodies, separated by immense "distances, but must likewise act between their mi-"nute particles at small distances, and consequently "be concerned in chemical phenomena." The discovery by Berthollet, that the intensity of chemical action is influenced by quantity of matter, still farther

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* *Histoire Naturelle*, tom. xxvi., (*seconde vue de la nature*).

† Chemical Dictionary, article *Gravity*.

favours the supposition, that the different varieties of attraction are the same power, modified by the circumstances under which it operates.

It must also be admitted, however, that no case of affinity has been demonstrated from the general law of attraction, modified by any assumption with regard to figure; and these speculations, whatever probability they may have, are still not sufficiently precise to serve as the basis of any theory. And as we are altogether unable to ascertain the figures and positions of the particles of matter, the laws of contiguous attraction cannot be deduced from any general principle, but must necessarily be inferred from the observation of its effects.

Contiguous attraction may be exerted, either between the particles of the same kind of matter, or between particles of different kinds. In the former case, it is named the attraction of aggregation or cohesion; in the latter, chemical attraction or chemical affinity. There appears little reason to doubt but that these are ultimately the same power, the different effects produced by their action arising from the difference in the particles they unite. In the one case, the particles being of the same kind, must form an aggregate possessed of their general properties; in the other, the particles being dissimilar, must by their union, have their properties more or less changed. Admitting their identity, however, the effects they do produce, are so different, that they require to be considered apart. The phenomena to which they give rise, and the laws they observe, will be the subjects of the two following chapters.

CHAP. I.

OF THE ATTRACTION OF AGGREGATION OR COHESION.

AGGREGATION, or that attraction exerted between particles of the same kind of matter, is a force frequently concerned in chemical phenomena. It powerfully modifies the exertion of chemical attraction, and is an antagonist to the action of heat or caloric. Hence its effects are, to a certain extent at least, subjects of chemical investigation.

The existence of this attraction is very easily demonstrated. If two particles of a similar kind, sufficiently fluid to be susceptible of motion, are made to approach, when within a certain distance, they exert a mutual attraction, in consequence of which, they unite together; and this attraction retains them united, or opposes resistance to any force, the tendency of which is to occasion their separation.

In a solid mass of matter the exertion of this power is still stronger. The particles which compose the mass are united by a reciprocal attraction, so powerful that they are not capable of being moved, with regard to each other, by any mechanical agent; and a much stronger resistance is opposed to their disunion.

In substances, on the contrary, existing in the state

of vapour or of air, this power is entirely negative. The particles, instead of attracting, repel each other; they are made to approximate only by pressure applied to them, and they recede in proportion as that pressure is withdrawn.

Bodies exist, therefore, in the aëriform, the fluid, or the solid state, according as this mutual attraction is exerted between their particles. In the aëriform state, its force is entirely overcome. In the state of fluidity it is exerted, but so weakly that the slightest impulse is sufficient to disunite the parts of which the fluid is composed; and scarcely any resistance is opposed to any force, the operation of which is to bring them into new arrangements; nor in different fluids can we perceive much difference in the degree of their cohesion. In the solid state, it is so far energetic as to oppose considerable resistance to any power tending to separate the particles, or cause them to move with regard to each other; and in different solids, we discover it to be exerted in very different degrees of strength.

Several qualities of solid bodies appear to arise from peculiarities in the arrangement of their particles, according to the mode and the degree in which aggregation is exerted, or in which it is balanced by the repulsive power of caloric, such as their tenacity, elasticity, and hardness.

Aggregation is weakened in bodies, or entirely overcome by two causes,—by the operation of heat, or by the exertion of a mutual attraction between two kinds of matter.

If we expose a solid substance to a moderate degree of heat, its volume is enlarged; the particles composing it, therefore, are so far separated from each other, and of course the attraction by which they were kept in union is counteracted. The enlargement of volume continues to proceed, in proportion as the heat is increased, until the point is reached at which the attraction is so far weakened that the body passes into the fluid form. If the application of heat be still continued, the particles of the fluid are equally separated from each other; and this continues increasing, until the attraction between them is entirely overcome, and the fluid passes into the aërial form.

The same changes may likewise be produced by the exertion of chemical affinity. Thus, if a liquid be poured on a solid substance, it in many cases happens, that a mutual attraction is exerted between the two bodies, in consequence of which, the aggregation of the solid is subverted, its particles are detached, and uniformly diffused through the liquid, so as to be no longer perceptible, and not even to impair the transparency. This constitutes the chemical process named Solution. And as cohesion is weakened by a high temperature, it is obvious, that the application of heat must favour solution, by diminishing that resistance which is opposed to the affinity by which it is effected,—a law which is accordingly observed. The affinity exerted to a solid by a substance in the aërial form, may likewise overcome its cohesion, and cause it to pass into the aëriform state.

When these powers, whether of heat or chemical af-

finity are withdrawn, cohesion resumes its force, or the body returns to the solid form. By diminishing heat sufficiently, an aërial body may be reduced to the state of fluidity; and all fluids, by sufficient cooling, may be rendered solid. The suspension of chemical affinity, in other cases, gives rise to the same changes of form, or a solid may be deposited from a liquid, or air, in which it had been dissolved.

When the attraction of aggregation is thus exerted, the particles are sometimes united indiscriminately, so as to form irregular masses; sometimes they pass into peculiar arrangements, whence masses of regular and determinate figures arise.

The former happens generally when the attraction has been exerted suddenly, and with considerable force. If a fluid, which has been melted by heat, be suddenly cooled, a mass is formed altogether irregular. Or if, in consequence of chemical action, a substance be produced, the particles of which have a strong mutual attraction, this is exerted at the moment of its production, and the substance is separated in the form of a powder. This latter case is named in chemical language Precipitation, and the substance is said to be precipitated.

But if the attraction of aggregation which has been weakened, either by the operation of heat or of a chemical affinity, resume its force more slowly or equably, the particles are not united indiscriminately, but in uniting assume a particular arrangement, and thus form masses of regular figures, or bounded by plane surfaces and determinate angles. When aggregation

is exerted in this manner, and with this result, the operation is named Crystallization, and such regular figured masses are denominated Crystals. As a chemical operation of considerable importance, it requires to be more fully considered.

Crystallization is of two kinds: first, as it takes place from the reduction of temperature, in a body which has had fluidity communicated to it by the operation of heat; and, secondly, as it proceeds from the diminution in the solvent power of a fluid, which has communicated fluidity to a solid, by having combined with it.

Of the first kind of crystallization, water affords an example, in passing into ice by a reduction of its temperature. At first long and slender spiculæ form in the fluid, and from these others shoot out at a certain angle, and this continues till the interstices are filled with these crystals, and the whole becomes a solid transparent mass. We have also examples of it in the metals, which, when melted and cooled slowly, assume symmetrical forms. Some inflammables, as sulphur, crystallize in a similar manner.

Of the second kind of crystallization, the principal examples are derived from the order of salts, and a few other solids soluble in water; and with regard to this, several facts of importance require to be stated.

The solution of a solid in a fluid, it has been remarked, is, in almost every case, increased by heat, which weakens cohesion: hence a larger quantity of the solid is kept in solution at a high than at a low temperature. If we prepare, therefore, a solution of

a salt in hot water, the solution being saturated, or the fluid having dissolved as much of the salt as it can do, on allowing it to cool, the portion of salt which the heat enabled the fluid to dissolve, will separate; and unless the cooling of the solution has been very rapid, the particles of the solid, in approaching to each other, will pass into those regular arrangements which constitute crystals.

The same result will be obtained by withdrawing part of the fluid by which the solid is dissolved. If this be done slowly, or by spontaneous evaporation, the particles will obey the law of attraction which unites them in regular forms; and crystals are in this way formed, frequently more regular and of a larger size than by the former method of reducing the temperature of the solution. Some can be crystallized only in this method.

In both cases, the fluid in which the crystals form is still a saturated solution of the solid, and by a farther evaporation, joined sometimes with subsequent cooling, will again crystallize.

In general, it holds true, that the slower the formation of a crystal, the more perfect is its symmetrical arrangement; it is also larger, harder, and more transparent: while, when the process is too rapid, or is disturbed by agitation or other causes, the arrangement is less regular, and the form incomplete. Hence the crystals formed in nature are in general so much more perfect than those produced by artificial processes.

Crystallization is promoted by affording a nucleus,

or solid point at which it may commence, and still more so if a crystal be introduced into the solution. Crystallization immediately commences from it, if the solution be a saturated one, and it is even capable of causing a part of the solid to be separated which the water at the temperature at which it takes place could have retained in solution. Even the regularity of the figure of this crystal seems to have an effect in rendering the crystallization more or less regular; and on this Le Blanc has founded a method of obtaining large and perfect crystals. It consists in selecting very regular crystals of a salt that have been newly formed, and putting them into a saturated solution of the same salt. They increase in size; and as the side which is in contact with the vessel receives no increase, they are to be turned daily, to preserve their regularity. After some time, the largest and most regular of these crystals are to be selected, and the same process repeated on them; and thus crystals much larger, and more regular than are usually formed in a solution, may be obtained *.

The access of the air has an important influence on this process. If a saturated solution of salt, while hot, be put into a vessel from which the air is excluded, it does not crystallize even when cold. But if the air be admitted, the crystallization immediately commences, and proceeds with rapidity. It has been shewn by Dr Higgins, that any pressure, equivalent

* *Journal de Physique*, tom. lv. p. 300.

to that of the atmosphere, as the pressure of a column of mercury, has the same effect *.

This last fact leads us, of course, to regard the agency of the air in promoting crystallization, as depending on the pressure it exerts; and although it has not been explained how this influences the process, the following may perhaps be admitted as a probable theory. When the saturated solution of the salt is inclosed in the vessel, and the pressure of the atmosphere excluded, the particles in solution may be conceived as placed at distances too great to admit of the attraction of cohesion being exerted, so as to cause them to unite and crystallize. But when the pressure of the air, or any equivalent pressure, is brought to act on the surface of the fluid, its particles, as well as the particles of the solid contained in it, are forced nearer to each other; the distances between them are lessened; the attraction of cohesion is exerted, and the crystallization commences. The small crystals that are thus formed at the surface afford solid points from which other crystals are formed, and this proceeds rapidly through the whole fluid.

During crystallization a quantity of heat is rendered sensible: this is more apparent in the experiment just stated, from the rapidity of the crystallization. In many cases, the volume of the substance crystallizing is enlarged, as in the example of water, of iron,

* Minutes of a Society for Philosophical Experiments, p. 89.

and of the greater number of salts; but in others the volume is diminished. Quicksilver, in congealing, contracts about $\frac{1}{2\,3}$ of its whole bulk, yet it exhibits the crystalline texture; and when the congelation is partial, the crystalline figure can even be discovered.

Crystals deposited from water always contain a quantity of it, which is retained by the affinity of the solid, and has passed with it into the concrete form. It is termed Water of Crystallization. Its quantity is very various; sometimes it equals or exceeds the weight of the solid, and sometimes it amounts only to a few parts in the hundred. Much of the cold produced during the solution of salts in water, is owing to this water of crystallization passing into the fluid state: hence crystallized salts generally produce more cold than when they are uncrystallized. If the water of crystallization be expelled from a crystal, it loses its transparency, and at length its form. Crystals which part with their water of crystallization when exposed to the atmosphere, are said to *effloresce*, and to *deliquesce* when they attract water and become humid.

Some substances have so strong an affinity to the fluid in which they are dissolved, or so little tendency to cohesion, that they do not crystallize. In some cases, their crystallization may be effected by adding to the solution a substance exerting an affinity to the fluid, and of course weakening its affinity to the solid it holds dissolved.

As different bodies require very different quantities of water for their solution, it is possible when two such bodies are dissolved in one fluid, to obtain them

separate by crystallization, the one which is least soluble, or most disposed to crystallize, first passing to the solid form; and, by farther evaporation, the other is obtained. A fact on this subject, somewhat singular, is noticed by Mr Kirwan. If into a saturated solution of two salts in water, a crystal of either be put, that salt crystallizes in preference to the other.

By crystallization, also, salts, the solubility of which in water is unequally promoted by heat, may be obtained separately from the same solution. Thus, if one salt be much more soluble in hot than in cold water, and another be equally soluble or nearly so at any temperature, on evaporating the solution sufficiently, the latter salt will crystallize while the liquor is hot; on cooling, the other will shoot into crystals; and, by alternate evaporation and cooling, the two may be obtained uncombined, though generally with a little intermixture of each other.

Sometimes, however, when two salts are in solution in the same fluid, and have even different tendencies to crystallization, their mutual affinity leads them to crystallize in one mass, and even to assume a form different from that in which separately they would have crystallized.

In other cases, this mutual affinity between substances in solution is sufficient to resist their crystallization, or to render it more difficult.

Crystallization sometimes takes place when bodies in the aërial form become subject to the attraction of aggregation; and even solids separated from a liquid

by chemical action, in some instances, in the moment of their separation, assume a crystallized form.

The theory of crystallization is still obscure, so far at least as relates to the cause of the regular forms to which it gives rise. This has been accounted for, on the supposition that the particles of different bodies have different figures, and that the particles of each crystallizable body have a polarity or a tendency to arrange themselves in obeying the law of cohesion, by certain sides in preference to others. The uniformity of crystallization in each individual, and the difference in the figure of its crystals from that in others, are thus explained. But the explanation has not sufficient precision to claim the name of a theory.

Every substance in crystallizing is disposed to assume a particular figure. Thus, sea-salt crystallizes in the form of a cube; nitre in that of a hexaedral prism; sugar in that of a four or six sided prism with triedral terminations. The crystalline figure in any substance, however, is not invariable, but may be altered by circumstances affecting the crystallization; and we find the same substance crystallized under a variety of forms. Sea-salt crystallizes not only in cubes, but also in octaedrons; and carbonate of lime is found in nature in the form of an hexaedral prism, an hexaedral and a triedral pyramid.

Hauy has succeeded in developing the theory of the structure of crystals, so far as to shew, that in every crystallized substance, whatever may be the difference of figure, which may arise from modifying cir-

cumstances, there is, in all its crystals, a primitive form, the nucleus as it were of the crystal, invariable in each substance, and, by various modifications which he points out, giving rise to the numerous secondary or actually existing forms.

Romé de L'Isle had conceived the idea, that all the varieties of crystals with which we are acquainted might be derived from certain primitive or simple forms, by the different truncations of which these forms are susceptible. Thus, to take the most simple example, a cube may be truncated in the direction of its sides, its angles, or edges. If the angles be cut off, we shall have no longer a figure of six sides, but of fourteen; if the edges be struck off, they will be replaced by twelve faces, and the figure will now have eighteen sides; or, lastly, if the cube be truncated in the direction parallel to one of its faces, the equality of its sides will be destroyed, and a rectangled parallelopipedon be produced; and these new forms will admit of other truncations, giving rise to a great diversity of figures. A view of these truncations, conveying, of course, a general idea of the system of Romé de L'Isle, is given Plate I. Fig. 1. represents a cube: Fig. 2. a cube truncated on the angles: Fig. 3. a cube truncated on the edges: Fig. 4. a cube truncated in the direction parallel to one of the faces. It is obvious, that this may be carried farther, so as to give rise to other figures. The last, for example, may be truncated on its edges or angles, and other varieties may arise from these being combined, as

from truncations both of the angles and edges at the same time *.

In this manner De L'Isle prosecuted the modifications of what he conceived to be the more simple forms, shewed how these might give rise to immense varieties of crystalline figures, and traced them, by easy gradations, from the primitive figure to others so remote as scarcely to appear to be allied to it. The forms which he regarded as primitive are the tetraedron, the cube, the rectangular octaedron, the rhomboidal parallelopipedon, the rhomboidal octaedron, and the dodecaedron with triangular faces †.

The primitive forms which Romé de L'Isle had assumed, were, however, altogether arbitrary, and were selected merely from their supposed simplicity. Nor were the truncations less hypothetical, by which the transitions of these into secondary forms were explained. Hauy, by a happy discovery, has demonstrated, where Romé de L'Isle had merely imagined; he has detected the primitive form by mechanical analysis, and has established a real instead of an arbitrary, though descriptive system of crystallography. I shall give an abstract from his Treatise on Mineralogy of this important system.

Gahn had observed, that in breaking a pyramidal crystal of carbonate of lime, it afforded rhomboidal fragments, of which it appeared to be entirely formed. Bergman from this conceived the idea, that in

* Tab. Crystallograph.

† Crystallographie, t. i. 74.

every crystal there exists a primitive form, from which the actual forms, having often no resemblance to it, may be generated, by the superposition of decreasing laminæ; and that, by the mechanical division of crystals, according to those joinings which yield with most facility to a mechanical force, this form may be detected, and the laws by which it gives rise to the different crystals determined *. This is the basis of the system of Hauy. He demonstrated what Bergman had scarcely more than imagined. He discovered the particular laws of decrements which are observed, shewed how from these all the secondary forms might be derived, and how the primitive form may be detected, either by calculation or mechanical division.

The fact which led to these views is, that crystals can be mechanically divided only in certain divisions, so as to afford smooth surfaces,—a fact long known to those who work on the gems. Suppose we have a crystal of calcareous spar, a regular hexaedral prism, represented in Plate I. fig. 5. and 6. †, if we endeavour to divide it parallel to the edges, which form the outlines

* Physical and Chemical Essays, vol. ii. p. 1.

† In these and the other plates representing the crystalline forms. the entire lines represent the edges or outlines of that part of the solid immediately presented to view, and the dotted lines those situated in the opposite part, which of course are visible only in supposing the solid diaphanous.

of the basis of the prism, we shall find that three of these edges, taken alternately at the upper extremity, the edges *l f*, *d c*, *b m*, readily yield to this division, by a knife struck in the proper direction; but that the other three, those which are intermediate, *f d*, *c b*, and *m l*, cannot be divided in a similar manner; and if broken by a greater force, the fracture, instead of being polished like the others, is rugged and uneven. If we repeat the experiment at the under extremity of the prism, we shall find here also, that segments of three only of the edges can be detached; but these edges, instead of being the corresponding ones with those divisible at the upper extremity, that is, *l f*, *c d*, *b m*, are the intermediate ones, *f d*, *c b*, and *m l*.

The six divisions expose so many trapeziums. Three of these are represented in fig. 6., namely, the two which cut off the edges *l f*, *c d*, represented by the dotted lines *p p*, *o o*, and *a a*, *k k*, and that which cuts off the inferior edge, *d*, *f*, and which is marked by the dotted lines *n n*, *i i*.

Each of these trapeziums will have a smoothness and lustre, from which it can be perceived that it coincides with one of the natural joinings, the assemblage of which forms the prism. The prism cannot be divided in any other directions than these. But if the division be continued parallel to the first segments, it necessarily happens, that on one hand the surfaces of the basis of the prism become narrower, and that, on the other hand, the heights of the sides diminish; and at the point at which, continuing the sections, the bases disappear, the prism will be changed

into a dodecaedron with pentagonal faces (fig. 7.); six of which, *o o i* O *e*, *o* I *k i i*, &c. are the remains of the sides of the prism, and the other six, E A I *o o*, O A, K *i i*, &c. are the immediate results of the mechanical division *.

Beyond this point, the planes at the extremities preserve their figure and dimensions, while the lateral planes continue to diminish in height, until the points *o*, *k* of the pentagon *o* I *k i i* coinciding with the points *i*, *i*, and also the other points similarly situated, having a like coincidence, each pentagon is reduced to a simple triangle, as is represented in fig. 8.

Lastly, by continuing the sections, the triangles are made to disappear, so that there remains no vestige of the surface of the original prism; but, in place of it, we have the obtuse rhomboid E A I O, (fig. 9.), which is therefore the nucleus, or primitive form †.

This discovery of the method of dividing a crystal was made by Hauy, in examining a crystal of calcareous spar, which had been detached from a group of which it formed a part. He observed, that the fracture had happened at one of the edges of the base of the prism, and that its surface was perfectly smooth

* In this and the two succeeding figures, the hexaedral prism which circumscribes the solid, extracted from it in the division, is still represented, to shew better the progress of the operation.

† *Traité de Mineralogie*, tom. i. p. 21.

and regular. Attempting to detach a segment in a similar direction from the contiguous edge, he could not succeed, but the one next to it was easily divided; and proceeding in this manner, he was able to effect the mechanical division of the crystal in the manner already explained. Struck with the important result of the experiment, he applied the same method to other crystalline forms of the same substance, and obtained from them the same result; the crystal, whatever was its figure, being by this mechanical division converted into a rhomb. Thus, in the dodecaedron composed of two six sided pyramids, joined by the base, the primitive form may be obtained at once, by making a first section on the edges E O, O I, fig. 10.; a second on the edges I K, G K; a third on G H, E H; a fourth on O I, I K; a fifth on G K, G H; and, lastly, a sixth on E H, E O; and the result is, that these edges become the same with the lateral edges of the primitive form, as may be perceived from mere inspection of fig. 11., which represents this primitive form inscribed in the dodecaedron. He then applied it to other crystalline substances, and found, that from these also, by discovering the joints by which the laminæ composing the crystals are united, a certain primitive form might be extracted. That of fluor spar is an octaedron; that of the heavy spar a prism with rhomboidal bases; of corundum a rhomboid somewhat acute; of beryl a hexaedral prism; and of the Elba iron-ore a cube. Each of these forms is constant with regard to the species, and is that from which all the forms of the varieties, often extremely

numerous, are derived. The latter are denominated by Hauy secondary forms. Sometimes, though rarely, the primitive and secondary forms are the same.

It is not every crystallized substance, however, that admits of this mechanical analysis. But, with regard to those which have hitherto refused it, Hauy has remarked, that their surface striated in a certain direction, or the relation subsisting among the different secondary forms of the same substance, afford indications which lead to the determination, with at least much probability, of their primitive forms.

Such is the process by which Hauy establishes what he names the Primitive Form of Crystals, and which he defines, "A solid of a constant form, inserted sym- "metrically in all the crystals of the same species, "and the faces of which observe the directions of the "layers which compose these crystals." The primitive forms hitherto observed are reducible to six: —the parallelopipedon, which includes the cube, the rhomb, and all the solids which are terminated by six faces, parallel two and two; the tetraedron; the octaedron; the regular hexaedral prism; the dodecaedron, with equal and similar rhomboidal planes, and the dodecaedron with triangular planes.

Hauy carries the division of crystals still farther, however, than the primitive forms. The solid which constitutes it, is not the last term of the mechanical analysis; it may always be still farther subdivided, parallel to its different faces, and sometimes even in other directions. All the enveloping matter is equally divisible, by sections parallel to the faces of the

primitive form; and the only limit to this possible division, is that placed by the composition of the substance. The calcareous spar, to take it as an example, may be reduced to a particle, beyond which the division cannot be carried, without resolving it into its elements, lime and carbonic acid; or, at least, it may be reduced to a particle, beyond which, if its minuteness allowed us to operate upon it, it is demonstrable its figure would not change. To these last particles, the result of the mechanical analysis, Hauy gives the name of *integrant particles*, and their union constitutes the crystal. Their forms, so far as experiment has been carried, are three: the tetraedron, the simplest of pyramids; the triangular prism, the simplest of prisms; and the parallelopipedon, the simplest of solids which have their faces parallel two and two. There can be little doubt, that it is between these that the attraction of cohesion is immediately exerted.

The primitive forms and the figures of the integrant particles being determined, it remains, to complete the theory of the structure of crystals, to shew by what arrangements the secondary forms, in other words, the actually existing crystals, are produced.

The nucleus of the crystal is the symmetrical solid which constitutes its primitive form, arising from the union of the integrant particles, either by their faces or their edges; and the additional matter which forms the crystal consists of layers of these particles, superadded to that nucleus, and arranged on its faces; and to account for the formation of the crystal under a figure different from that of its primitive form, these

layers, as they recede from it, are supposed to decrease in the space they occupy, from the regular abstraction of one or more ranges of the integrant particles. This decrease may take place in various modes; and according to these, different figures of crystallization will be produced.

Thus, to take the simplest example, let it be supposed that the primitive form is a cube; it is easy to conceive, that on each of its six sides may be reared a series of decreasing layers or laminæ, composed entirely of cubical particles, each layer diminishing on each of its edges by one row of the minute cubes of which it consists. The laminæ thus decreasing as they recede from the base on which they rest, until the apex consists of a single particle, it is obvious, that on each side of the cube a four-sided pyramid will be formed. Two of these are represented, (fig. 12), A B C D, G B C G.

We shall thus have, then, six four-sided pyramids, and of course twenty-four triangles, such as A B C, B C E, C E G, &c. But since the decrease is uniform on all the sides, as from the line B C to A, and from the same line to E, it must also be uniform from A to E; it is obvious, therefore, that the side A B C, of the one pyramid will be found exactly in the same plane as the side B C E of the adjacent pyramid; so that the entire surface of these will be the rhomb A B E C. The case must be the same with all the others; the twenty-four triangles will therefore be reduced to twelve rhombs, and the figure will be a dodecaedron, very remote from the primitive form.

Now, a crystal of this figure, and having this primitive form, would be resolved into that form, merely by cutting off the six solid angles by sections in the direction of the small diagonals of the sides which go to the formation of these angles. We should thus successively uncover six squares, which will be the faces of the primitive cube.

In explaining this structure of a crystal, although the representation in the figure be such as to shew the decrease of the laminæ, by rows of particles of such a size as to give a surface uneven, similar to a succession of steps, it is obvious, that if we substitute for this the delicate structure of nature, the number of laminæ may be so great, and the minuteness of their cubical particles such, that the depressions or channels at their edges will be altogether imperceptible to our senses, and the surfaces will appear perfect planes.

Such is an example of the production of a secondary from a primitive form, by superposition of laminæ, decreasing according to a certain law. It is obvious, that the laws of decrement may be various, and accordingly the decrements stated by Hauy are of four different kinds: First, Decrements on the edges, or parallel to the sides of the primitive form, of which the above is an example. 2d, Decrements on the angles, that is, decrements of which the lines are parallel to the diagonals of the faces of the primitive form. 3d, Intermediate decrements, or those which are parallel to lines situated between the diagonals and edges of that form. 4th, Mixed decrements, in which the number

of ranges, abstracted in breath or in height, give proportions, the two terms of which are beyond unity.

These four laws of decrements, explain, by the modifications of which they are susceptible, the structure of all the varieties of form under which crystals are presented to us. These modifications are reduced to the following. 1st, Sometimes the decrements take place on all the edges, or on all the angles. 2d, Sometimes on certain edges or certain angles only. 3d, Sometimes they are uniform, by one, two, three ranges or more. 4th, Sometimes the law varies from one edge to another, or from one angle to another. 5th, In some cases the decrements on the edges correspond with the decrements on the angles. 6th, Sometimes the same edge or the same angle undergoes successively several laws of decrement; and, lastly, there are cases in which the secondary crystal has faces parallel to those of the primitive form, and which give rise to new modifications, from their combinations with the faces resulting from the decrements.

With such diversity of laws, the number of forms that may exist is immense, and far exceeds what have been observed. Confining the calculation to two of the simplest laws, those which produce subtractions by one or two ranges, it is shewn, that carbonate of lime is susceptible of 2044 different forms,—a number fifty times greater than that of the forms already known; and if decrements by three and four ranges be admitted into the combination, the calculation will give 8,388,604 possible forms of the same substance. And even this number may be much aug-

mented, in consequence either of intermediate or mixed decrements being taken into account.

To give a proper view of the applications of these laws of decrements would require a statement altogether inconsistent with the nature of this work, and the system must indeed be best studied in all its details. Having given a general outline of the theory, I must refer for these details to Hauy, *Traité de Mineralogie*, tom. i. ii. A full abstract of it is also given by the author in the *Annales de Chimie*, t. xvii., of which there is a translation in the first volume of the Philosophical Magazine; and it is developed in an excellent statement of it by Abbé Buée in Nicholson's Journal, vol. ix., octavo.

In concluding this sketch of crystallography, I have supposed it might be useful to give figures of the more usual forms of crystals, and the modifications to which they are subject, which will frequently be referred to in the progress of the work, and particularly in the mineralogical part of it. And as the minute details of Hauy would be misplaced in a work of this kind, I have given the terms and definitions which are employed by Werner, as these are much less remote from those that have hitherto been in established use.

It is necessary to premise, that the parts of which a crystal is conceived to be composed, are planes, edges, and angles. Planes, according to the usual geometrical definition, are surfaces lying evenly between their bounding lines: they are distinguished into *lateral*, which are considered as those parts of the surface of the body which are of greatest extent, and which form

its confines towards its smallest extent; and *extreme* or *terminal*, which are those of smallest extent, and form the bounds of the body towards its largest extent. Edges are formed by the junction of two planes under determinate angles; they also are *lateral*, or those formed by the junction of two lateral planes; and *terminal*, formed by the junction of two terminal planes, or of a terminal with a lateral plane. Lastly, angles are formed by the junction of three or more planes in one point.

Werner admits seven primary figures of crystals, which are susceptible of numerous modifications. These figures are, the icosaedron, the dodecaedron, the hexaedron which includes the cube and the rhomb, the prism, the pyramid, the table, and the lens:

1st, The icosaedron, Plate II. fig. 13., a solid, consisting of twenty equilateral triangular planes, united under equal angles: 2d, The dodecaedron, fig. 14., or solid, of twelve equal and regular pentagonal faces: 3d, The cube, fig. 15., or solid, composed of six quadrilateral planes, united at right angles: 4th, The rhomb, fig. 16., or solid of six quadrilateral planes, united at oblique angles: 5th, The prism, or solid of two terminal planes parallel, equal and similar, connected by quadrangular lateral planes, having one direction; the number of lateral planes may of course be various; the usual forms observed in crystals are the four-sided rectangular prism, fig. 17.; the four-sided rhomboidal or oblique angular prism, fig. 18.; and the six-sided equiangular prism, fig. 19: 6th, The

pyramid, a solid, the base of which is a plane of an indeterminate number of sides, and the sides triangles, the vertices of which meet in one point, forming the summit: the more common varieties of this figure, as forms of crystals, are the three-sided pyramid or tetraedron, fig. 20. Plate III., and the four-sided pyramid, fig. 21: 7th, The table, which, strictly speaking, is nothing but a very compressed prism; it is defined as composed of two parallel lateral planes, and of an indeterminate number of terminal planes, connected with the lateral planes and with each other, and small compared with the lateral ones; the principal varieties are the oblique-angular or rhomboidal four-sided table, fig. 22., the rectangular four-sided table, fig. 23., and the six-sided table, fig. 24: Lastly, The lens, fig. 25., a solid, consisting of only two planes, which are curved; of which there are two varieties, one composed of two convex planes, and another composed of a convex and a concave plane.

These simple figures are modified by combination, by truncation, by bevelment, and by acumination.

The modifications by combination are confined to the pyramid, and these are frequent, two pyramids being joined by the base; the lateral planes of the one being set either *directly* on the lateral planes of the other, as in the double four-sided pyramid, or octaedron, fig. 26.; or *obliquely*, as in the double four sided pyramid, fig. 27. Fig. 28. is the double six sided pyramid.

A crystal is said to be truncated, when any or all of its solid angles or edges appear cut off, so that

where there would have been an edge or angle, we have a plane, as has already been represented in fig. 2. and 3. These two figures represent forms arising from the truncation of the cube. Fig. 29. Pl. IV. shews the cube with both the angles and edges truncated: Fig. 30. the six-sided prism, with truncated terminal edges: Fig. 31. the same prism, with both the lateral and terminal edges truncated.

A crystal is said to be bevelled, when its edges, angles, or terminal planes are so altered, that instead of an angle, edge, or terminal plane, there appear two smaller converging planes, which terminate in an edge. Fig. 32. shews the cube with bevelled edges: Fig. 33. the three-sided pyramid, with bevelled edges: Fig. 34. the oblique four-sided prism, bevelled on both extremities.

Lastly, The forms of crystals are altered by acumination. This is that kind of alteration, in which, in place of the angles, or terminal planes of a crystal, there are three or more planes converging, and forming a point or edge: Fig. 35. shews the cube, with the angles acuminated by three planes, set on the lateral planes: Fig. 36. the rectangular four-sided prism, acuminated by four planes, set on the lateral planes: Fig. 37. the six-sided prism, acuminated by six planes, set on the lateral planes. This kind of modification is often described as consisting of the primary form, with pyramidal terminations.

The forms of crystals from the preceding modifications, are frequently still more altered, and rendered complicated, by being superadded or combined; and

by the extent of the modifications, one form frequently passes into the other. The figures of crystals are likewise rendered complicated by aggregation, two or more crystals of the same substance being more or less closely united.—For the more minute details on this subject, particularly as related to mineralogy, I must, however, refer to the translation by Mr Weaver, of the External Characters of Minerals by Werner, or the Treatise on the same subject by Professor Jameson.

CHAP. II.

OF CHEMICAL ATTRACTION OR AFFINITY.

WE are indebted to Newton for the first just views of the nature and extensive agency of this power. Having remarked, that besides those attractions which extend to sensible distances, "there may be others "which reach to so small distances, as hitherto escape "observation;" he reviews, in the 31st Query, at the end of his Treatise on Optics, and in some other parts of his works *, a number of chemical phenomena, and considers them as arising from an attraction of this kind. When one body combines with another, he supposes this to arise from an attraction exerted from the particles of the one to those of the other; when they refuse to unite, it is because no such attraction exists; those which act with most energy are those, as he supposes, possessed of the strongest attraction; and when a compound is decomposed by the agency of another body, this he regards as

* Letter to Mr Boyle on the Cause of Gravitation, and Observations on the Nature of Acids.

owing to an attraction having been exerted by that body to one of the principles of the compound, superior in force to the attraction which existed between them.

Geoffroy the elder, conceived the idea of ascertaining the relative forces of affinity among different substances, by observing the order of the decompositions they were capable of producing. Pursuing the path which he had pointed out, succeeding chemists were occupied in observing these forces, as exerted by the principal chemical agents. The observations which had thus accumulated, were ably reviewed and corrected by Bergman, by whom likewise many individual facts were ascertained, and more precision given to the general theory of chemical attraction.

Bergman's views were received with little subsequent modification, and nearly the whole system of modern chemistry rested upon them. But the late researches of Berthollet have exhibited the subject under very different aspects: equally profound and original, they will probably have a permanent influence on the theories of chemical phenomena; and in consequence of them, it has become necessary to alter materially the statement of the general doctrines of chemical attraction. Without attempting to enumerate its laws, which I believe cannot yet be established with precision, I have endeavoured to deliver the theory of affinities under the following general divisions. In the first, I have premised a few necessary definitions relative to attraction and its results. Under the second, I have taken a general view of the phenomena to which it gives rise. In the third is consi-

dered the operation of those circumstances by which its exertion is influenced, and its effects modified. In the fourth I have brought under view the modifications of affinities, resulting from combination. The fifth is devoted to the consideration of the limits which affinity observes. And under the sixth are placed the details which relate to the forces with which it is exerted. Under these divisions every thing relating to chemical affinity may be systematically arranged; and in a note, I have added those more minute details and illustrations, particularly in what relates to Berthollet's speculations, which could not well be admitted into the text.

Sect. I. *Definitions relative to Chemical Attraction, and its Results.*

Chemical Attraction may be defined, That force by which the particles of heterogeneous bodies, when brought into apparent contact, have a tendency to unite intimately, and by which they are retained in a state of union, forming not a mere aggregate or mixture, but a new substance, in which the properties of the particles combined are more or less changed. From gravitation it is distinguished by not operating on masses of matter, nor at sensible distances, but by being confined in its action to the minute particles of matter: from cohesion, by being exerted always between particles of different kinds, and forming generally substances with new properties. The

term affinity has also been introduced, to denote this power. Affinity, therefore, is synonymous with chemical attraction.

This force appears to be elective, or it is not exerted indifferently by any body towards every other. Between many substances no mutual chemical attraction is apparent, or their particles cannot be brought into intimate and permanent union. It is uncertain, however, whether this is owing to their not having a mutual attraction, or whether it may not rather be ascribed to the predominance of circumstances by which this attraction is counteracted. By each body, too, it is exerted towards a series of others, with different degrees of force; and with regard to this also, there is reason to believe, that much of the difference is owing, not to real differences in the intensities of affinity, but to the operation of modifying circumstances.

The result of the exertion of chemical attraction between two bodies, is their intimate union, or assimilation into one substance, in which neither of them can be recognized, nor can they be again separated from each other by any mechanical force. This operation is denoted in chemistry by the term *Combination* or *Synthesis*. If we pour a quantity of water on common sea-salt, the particles of the salt, though heavier than the water, will be gradually attracted by it, and uniformly diffused through it, nor can they be again separated but by chemical agency. If we mix together a little lime and sulphur, and expose them to heat, a substance will be formed in which the two ingredients are intimately blended, and the properties

of which are totally dissimilar to those either of the sulphur or the lime. In both these examples, an affinity has been exerted between the substances concerned, and they have *combined* together.

Chemical combination, then, is that case where two or more different bodies are united together, in such a manner that they do not spontaneously separate, and cannot even be separated by any mechanical force. So intimately are the particles of the bodies which have combined, blended together, that if the smallest portion of the substance they have formed be examined, it will be found to consist of the same principles united in the same relative proportions as the general mass; and by this intimate union, the properties of both are altered, and new properties acquired.

Combination is to be distinguished from *mixture*, in which dissimilar particles are blended together, more or less intimately, but without being united by any attraction,—in which, therefore, no new qualities are acquired,—in which the difference of parts is easily discovered, and these parts are capable of being separated by mechanical means. It is also to be distinguished from *aggregation*, which is merely the union of particles of the same kind of matter, forming an aggregate, uniform in composition, but possessing all the properties of the particles of which it is composed.

The substance resulting from a chemical combination is denominated a Compound. The substances existing in it, or forming it, are named its Component or Constituent Parts. When these are again separated

from their union, the process is named, in chemical language, *Decomposition* or *Analysis.*

From these definitions, it is obvious, that all the varieties of matter, must, in a chemical point of view, fall to be considered as simple, or as compound. Either they must be resolvable into two or more different substances, from the union of which they have been formed, and in this case their composition is obvious, and they rank as compounds; or they must be incapable of such an analysis, and they are then regarded as simple or elementary. The great object of chemistry is to investigate the constitution of bodies—to determine what substances are simple, what compound; to trace the combinations into which the former are capable of entering; to decompose the latter, or discover of what constituent parts they are formed.

In investigating the actions exerted between the minute particles of matter, it is of importance to distinguish between them, as acted on by the force of aggregation, or the force of chemical affinity; and to facilitate this, the distinction has been introduced of the *integrant* and *constituent* particles of bodies. The constituent or component parts, are substances differing in their nature from each other, and from the substance they form. The integrant parts are precisely similar to each other, and to the general mass which is composed by their union; or they are merely the smallest particles into which a substance can be resolved without decomposition; while decomposition is always implied in the division of a body into its

constituent particles. The integrant parts are united by the force of aggregation, the constituent parts by chemical affinity. It is evident that simple bodies consist entirely of integrant parts, all their particles being alike in their properties. Compounds, again, may be considered as consisting both of integrant parts, and of component parts or dissimilar particles. It has been supposed, that when an attraction is exerted between two compound substances, it is between their integrant parts, not their constituent principles, and that it is the combination of the former which constitutes the substance formed by their union. Berthollet, on the contrary, has made the supposition, and employs it as the basis of much of his reasoning, that an attraction exerted between two compounds is still exerted from their constituent principles or elements, and is merely the sum of their attractions, modified by the state in which they exist in the combination; an opinion, the probability of which we shall afterwards have to examine.

Sect. II. *Of the General Phenomena which arise from the exertion of Chemical Attraction.*

The exertion of an attraction between the particles of two bodies, is followed by their intimate union or combination; and the most common and also the most important consequence of such a combination, is a change in the properties of the bodies combined.

This change is in many cases striking and complete, or the compound formed is totally dissimilar in its qualities to either of the substances from which it has originated. The taste, smell, colour, form, density, and other physical qualities, and the chemical properties of fusibility, volatility, solubility, tendency to combination, and order of attraction in the compound, bear no resemblance to the same properties in its constituent parts. We cannot, therefore, from our knowledge of the properties of any body, infer with certainty what will be the properties of the compound formed by its union with another.

From this change being so general, it has been established as a law of chemical attraction, and it is one perhaps to be admitted as just, that *when chemical combination has taken place, the compound which is formed does not possess properties merely intermediate between those of its component parts, but has acquired others more or less new.*

This law of chemical attraction is of vast importance, since it is from it that the properties of the greater number of material bodies are derived. Almost all the productions of nature are compounds formed from the union of a few simple substances; and the numerous properties they possess, adapting them to so many purposes of utility, are derived from this source. They retain not the properties of their simple elements, for these must be comparatively few, but derive new properties from the arrangements into which their principles are brought when they are combined together.

In consequence of this law, too, chemical action frequently exhibits very striking results; substances being formed or evolved in our experiments, which have properties totally different from those on which we have operated.

Of the changes which happen from chemical combination, none is more common than change of form, or of the state in which bodies exist. If two airs are combined together, the result is often a substance in the fluid or solid state. Two fluids united will form a solid; and when a solid is combined with a fluid, the compound more frequently exists in the fluid than in the solid form.

This last case is indeed so general, that a particular term has been applied to it in chemical language. Combination is the general term expressive of the union of substances from the exertion of mutual attraction; and the particular operation in which a solid is combined with a fluid, so that the fluid form is retained by the compound, has been denominated Solution. It has been conceived, that in this case the fluid is the active principle; it is said to dissolve the solid; or the solid is spoken of as dissolved by the fluid, or, as it is named, the solvent or menstruum. The attraction, however, whence the combination proceeds, is reciprocal; nor perhaps is there any propriety in the distinction of this from other cases of chemical union. It is one, however, very generally observed.

Though we have considered the change of properties from chemical action, as striking and important,

it is not to be understood that it is invariably so. In many cases the change is far from being considerable, or the properties of one or both of the substances united, can be recognized in the compound. In all the combinations, for example, of metals, with each other, the compound still retains the general metallic properties, though not precisely the same as in their constituent metals. And in the solutions of salts, and of many vegetable and animal products, in water or in spirit, the properties of the substances dissolved, with the exception of the form, are scarcely sensibly altered. Yet these are real chemical combinations; the substances are intimately blended, notwithstanding the difference of their specific gravities; and their union is permanent, or they cannot be disunited but by the operation of heat, or the exertion of superior affinities.

From the consideration of this class of facts, the older chemists even advanced the opinion that the properties of compounds are intermediate between those of their constituent parts; an opinion, the fallacy of which is demonstrated by the most general view of chemical combinations. In opposing it, some modern chemists have erred on the other extreme, by teaching that the properties are uniformly and completely different. The proper enunciation of the law is, that a change of properties more or less considerable is the consequence of chemical combination.

Berthollet has on this subject in some measure revived the older opinion, and has supposed, that in every case the properties of compounds are derived

from those of their constituent parts. But he has rendered it much less liable to exception, by assigning certain causes by which the properties are modified, and which are frequently so powerful as totally to disguise them. Thus opposing properties weaken or neutralize each other, and important changes are frequently produced in bodies combining together by the mutual penetration and condensation which accompany their combination. If, therefore, a combination be not of the most intimate kind, the properties of the elements may be expected to remain to a great extent in the compound, as they may also when the substances combined have few opposing or incompatible properties. But, in combinations of an opposite description, the properties may be expected to undergo a much greater change, though even in these the properties of the elements may often be recognized in those of the compound. A review of chemical phenomena will afford a number of facts which strictly accord with these conclusions. Note (A a).

In those combinations, in which the changes of properties are least considerable, we still in general find one change which perhaps accompanies every case of chemical union, and which may even be regarded as a test of it—an alteration of density; the density of the compound not being the mean of the densities of the component parts, and the deviation from this mean being even often considerable.

In the greater number of cases, the density is increased, or a mutual penetration appears to attend the combination. Where two airs, by combining,

pass into the fluid state, or when two fluids, or a fluid and solid, form a solid compound, this is necessarily the case to a great extent, and often the density not only exceeds the mean, but exceeds much that of the more dense of the combining substances.

In other cases, the augmentation of density is much less considerable, and is only somewhat superior to the mean density of the substances combined. If ardent spirit, of the specific gravity of 825, be mixed with an equal weight of distilled water, the specific gravity of which is 1000, the density of the fluid resulting from the combination of equal parts of the spirit and water is not the mean density 914, but is 930.

There are many similar examples in the combination of saline substances with water, in which a mutual approximation of the particles takes place. It follows from this, that the specific gravity of any compound fluid cannot be determined by calculation from the specific gravities of its ingredients, but must be ascertained by actual experiment.

A fact on this subject, somewhat singular, was observed by Mr Kirwan. It is, that in a combination, the increase of density frequently does not at once acquire its *maximum*, but continues to increase, though apparently the combination is made at once, and without any resistance. Thus, in combinations of sulphuric acid, or of nitric acid with water, he at first supposed, as any chemist would have done, that the full density is attained after the heat arising from the combination has been reduced, and the fluid has attained the temperature of the surrounding medium; yet he

found, that after the mixture had remained six hours, a time more than sufficient to cool it, its density still continued to increase; and that in combining one part of sulphuric acid with two of water, twelve hours at least were requisite to the combination attaining its full density *.

Another singular fact attending those combinations, in which there is an augmentation of density, is that the increase is greater when they are combined together at a low than when combined at a high temperature. This was ascertained by De Luc to be the case with alcohol and water, and by Dr Crawford to hold true also with sulphuric acid and water †.

Though there is a tendency, however, to increased density from combination, this is not always apparent. There are cases in which the density is, on the contrary, diminished. In every instance, perhaps, in which two liquids combine, the density is increased, and the same change follows from the intimate combination of two airs. But when a solid is dissolved by a liquid, the enlargement of volume which the solid acquires by passing into the fluid state, is sometimes greater than the condensation resulting from its union in that state with the liquid, the affinity of which has overcome its cohesion, and dissolved it. Hence, on the whole, an increase of volume or diminution of density

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* Philosophical Transactions, vol. lxxii. p. 180.

† Treatise on Heat, p. 480.

is the result *. We observe this in the solutions of a considerable number of salts in water. I must observe, however, that this diminution of density is not confined, as Berthollet has represented, to those cases in which there is a change of form. In a number of the combinations of the metals, the compound has a specific gravity inferior to the mean specific gravity of the metals combined, though it still exists in the solid state. In these cases, it is probable, that the enlargement of volume which happens, arises from a species of crystallization, which the alloy undergoes, and is similar to the increase of volume which attends the congelation of several substances.

The cases in which the changes of properties from combination are so inconsiderable, are generally those in which a solid combining with a fluid passes into the fluid form. This, as has been remarked, in chemical language, is termed Solution. Berthollet has extended the signification of the term,—applying it to all cases of chemical union, whether between a solid and fluid, two fluids, two airs, or an air and a fluid, which is not intimate, or where the attraction has not been sufficiently energetic to alter materially the properties of the substances united, but merely sufficient to overcome cohesion, elasticity, or any opposing force, and retain them united, without any intimate approximation of their parts.

As the affinity exerted by a solvent (or fluid dis-

* Berthollet's Statics, i. 169.

solving a solid,) to the body dissolved, is frequently so weak as not to give rise to any sensible alteration in the chemical relations of the body dissolved, it is often neglected in chemical reasonings, and regarded merely as communicating to the solid, that fluidity which favours the exertion of its attractions to other bodies. It is not always, however, to be viewed in this light; for, though it may differ in intensity from that which produces more powerful combinations, it is still often sufficiently energetic to modify the affinities of the substance dissolved.

Next to the change of properties, the most important phenomenon attending chemical action, is change of temperature, or in other words, the production either of heat or cold. This is so general an effect, that it has been established as a law, that *the exertion of chemical attraction is accompanied by a change of temperature*. In many cases it is considerable, and there are few examples of chemical action in which, when accurately examined, it will not be observed.

The production of heat is the more frequent change, and the great source of heat in the operations of art, is chemical combination. The heat evolved in combustion, in fermentation, and from the mixture of different chemical agents, has this origin.

In other cases of chemical combination, the temperature is diminished, or cold is produced. This happens in the solutions of salts in water, or in other fluids which act upon them with more energy than water does; and, in some of the latter solutions, very intense colds are produced. It happens to a still greater

extent, when the salts act on ice or snow; and the greatest colds we can produce arise from these combinations.

Wherever a production of heat is observable in chemical combination, we can trace an increased density accompanying it; and the evolution of heat may be ascribed to this condensation, since we know, that the mechanical condensation of a compressible body produces heat. On the other hand, where cold is produced in chemical action, there is always an enlargement of volume, to which, therefore, the cold may be ascribed.

But we do not find that the production either of heat or cold, from chemical action, is proportioned to the increase or diminution of density. Allowing the latter, therefore, to be the cause of the change of temperature, there must be some other circumstance by which it is modified. This is the change of form. It is sufficient, at present, to state, that when a body passes from the aëriform to the liquid state, or from the liquid to the aëriform state, it gives out heat, and in the opposite changes, absorbs it, in quantities not proportioned to the degree in which the density is altered by the form; and hence such transitions of form, when they accompany chemical action, which they frequently do, modify the production of heat or cold which arise from the condensation attending the combination itself. By taking into consideration these two circumstances, the production of heat or cold from chemical action, is explained with more precision than if

one of them only were admitted in the theory; and there can be no doubt, as matter of fact, that both, when they occur, have a share in producing the change of temperature. Note (A b).

SECT. III. *Of the circumstances by which the exertion of Affinity is influenced.*

IT had long been observed, that the exertion of chemical attraction among bodies is not uniform, but is, to a certain extent, influenced by circumstances. A number of facts proved, that the force of aggregation opposes combination, and that the agency of heat modifies not less powerfully the forces of affinity. This part of the subject has, however, been considered under a much more extensive point of view by Berthollet; and this section will include principally a statement of so much of the old doctrines as appear to be just, combined with the views he has delivered. The circumstances he enumerates, as influencing the exertion of attraction, are, Quantity of Matter, Cohesion, Insolubility, Specific Gravity, Elasticity, and Efflorescence.

I. QUANTITY OF MATTER.—The attraction of gravitation acts on bodies with a force directly as the quantity of matter, and inversely as the square of the distance; but in chemical attraction, it is not possible to perceive the operation of such a law. It is exerted between bodies only when they are in apparent contact

with each other; and, consequently, we have it not in our power to ascertain accurately the effect of distance on the force with which it operates; though we find an approximation to the law, in the attraction becoming weaker as the distance between the particles is increased, and ceasing when it amounts to a certain extent. We find another approximation to it in the fact; that the force of affinity is modified by the relative quantity of the bodies brought within the sphere of mutual action, or, according to the statement of Berthollet, that "every substance, having a tendency to enter into combination, "acts in the ratio of its affinity and its quantity."

Some of the facts from which this law of chemical attraction is deduced, had been observed prior to the researches of this able chemist. It had been known, that the force of affinity between two substances, capable of combining in different proportions, is different in one proportion from what it is in another. It was clearly shewn by Bergman, that, in decomposing a compound by a superior affinity, a much larger quantity of the decomposing substance is frequently necessary than would have been calculated on in theory. It was observed, that in decomposing a compound by heat, or even by another attraction, the partial decomposition of it is often easily effected, while the entire separation of the one ingredient from the other is difficult or unattainable; and hence was deduced the law, That the force of attraction is in the inverse ratio of saturation, or that the particles which enter first into a combination, are retained by a stronger affinity than those afterwards combined. But little extension

was given to this principle, nor was its importance perceived. To Berthollet we are indebted for its full developement; for the application to chemical phenomena in general, of what had formerly been confined to individual facts; and for shewing, that, in all cases, combinations do not depend merely on affinity, but likewise on the proportions of the substances brought into action.

If affinity were an uniform force, different in its intensities, as exerted between different substances, and independent of quantity, it is evident, that when three substances, A B and C, having different affinities, are presented to each other, the two which exert the strongest attraction, suppose A and B, should combine together, to the perfect exclusion of the third C, and that C should remain completely isolated; and if the compound of A and B be exposed to the agency of C in any quantity whatever, it ought not to suffer any change, the circumstances, with the exception of quantity, being always supposed to be the same in these experiments. But, on the other hand, if the quantity of an ingredient adds to the force of its affinity, when three substances are presented to each other, two of them having attractions to the third, this third cannot be entirely combined with one, but must be shared between them, in the ratio of the affinity and quantity of each. Or if a combination of it with one of these substances, suppose with the one to which the attraction is strongest has been previously formed, on subjecting this compound to the agency of the third substance in large quantity, the affinity of this must be so far aided by

its quantity, as to occasion a partial decomposition, and abstract a part of the ingredient to which it has an attraction.

The truth of the doctrine, therefore, that affinity is modified by quantity, depends on the state of the fact with regard to these deductions. And, from the experiments of Berthollet, which stand uncontradicted, and which are confirmed by many collateral facts, they appear to be sufficiently established. It is shewn, in a number of cases, that a substance, when in large quantity, can partially decompose a compound, between the principles of which a stronger attraction exists, than the attraction it exerts to the principle with which it combines; that, on the other hand, when two substances are united together, by a comparatively weak affinity, and when the compound is subjected to the agency of a substance, having a stronger attraction to one of the ingredients, this substance cannot decompose the compound entirely; for, in proportion as the decomposition proceeds, the relative quantity of the other ingredient of the compound is increased, and, by aiding its affinity, is at length able to put a stop to the progress of the decomposition; that in both these cases, therefore, there is a partition of the base or subject of a combination between the two bodies whose actions are opposed, and that the proportions of this partition are determined as much by the difference of the quantities of the bodies, as by the difference of energy in their affinities. And what is the most simple proof of the proposition, a substance may be added in small quantity to a compound, without producing on it any sen-

sible effect, but if added in large quantity, will immediately decompose it.

From these facts, given more in detail, Note (A c), the conclusion may be drawn, that affinity is modified by quantity of matter, or *the chemical action of any body is exerted in the ratio of its affinity and quantity*.

From this law some important corollaries may be deduced.

First, It follows from it, that the chemical action of any substance on another, must diminish as it advances to saturation. Its energy depends on its affinity and quantity; that portion which enters into combination has its affinity saturated, and this being equivalent to its abstraction, the remaining quantity must, in conformity to the law, have a less powerful action.

Secondly, A substance subjected to decomposition, must oppose a stronger resistance to the decomposing agent, in proportion as the decomposition proceeds, from the increase in the relative quantity of the one ingredient of the compound, to the other which is abstracted. Hence, when a substance is separated from a combination by precipitation, it generally retains a portion of the substance with which it was combined; the proportion being determined by the force of the affinity between them, and the proportion of the substance by which the precipitation is occasioned. Yet there is not in every case this participation of a substance between two others exerting affinities towards it; but from the interference of cohesion or elasticity, decomposition is sometimes rendered complete, and

substances obtained pure and insulated. Thus the metals are precipitated from their solutions in their metallic state, and elastic fluids may be disengaged from a combination, without retaining any portion of the substance with which they were combined. Where these extraneous forces do not operate powerfully, this participation perhaps always takes place.

Lastly, It follows from this law, that in estimating the relative forces of affinity in bodies, the quantities of them must be taken into view, and ought to be equal.

II. Cohesion.—Cohesion, or that force by which homogeneous particles, or the particles of the same kind of matter, are held together, which, when exerted with energy, produces solidity, and when diminished, allows the production of the fluid and aëriform states, has an influence in counteracting affinity, and opposing chemical action, which has long been observed.

It is sufficiently evident that a force which retains the particles of a mass of matter in union, must oppose any force tending to separate them, in order to bring them into new arrangements or combinations, and the ultimate result must depend on the proportion of these forces to each other. Accordingly, from the opposition of these two powers in different degrees of energy, arise numerous shades of combination, more or less intimate, as the one predominates over the other, from the mere adhesion of the surfaces of bodies, or the absorption of a liquid into the interstices of a solid, to the most perfect chemical union. If cohesion

is powerful, a strong affinity may be effectually resisted, and no combination take place, though the bodies have a reciprocal attraction; and if cohesion be inconsiderable, a weak affinity may be predominant, and a combination be effected. The more powerful aggregation is, the stronger must a chemical attraction be to overcome it, and to unite the particles of two bodies together; and it equally follows, that whatever weakens aggregation favours combination.

There are, accordingly, a number of examples in chemistry, in which aggregation in bodies is so powerful, that they are not sensibly acted on by others, even in the fluid state, though the combinations of them are effected when the aggregation of the solid is destroyed. The native oxide of tin, it was known, resists the action of any acid; it was discovered by Guyton, that this apparent insolubility is owing merely to its strong aggregation, and that when this is overcome by mechanical operations, it becomes soluble. Klaproth found, that the ruby, the sapphire, and the adamantine spar, from the same cause,—the strength of the aggregation between their particles,—are scarcely affected by any chemical agent; but that, if their cohesion be destroyed, they are then acted on, and their analysis can be accomplished. Hence the mechanical operations of Trituration, Levigation, and Granulation, are of considerable importance in facilitating chemical action, partly by diminishing aggregation, and partly by increasing the surface on which affinity is exerted.

The observation of the effects of cohesion in counteracting chemical action, gave rise to the axiom which

has long been established in chemistry, *Corpora non agunt nisi sint soluta* : Bodies do not act on each other, unless they are dissolved, or in a fluid state. Though to this proposition there may be some exceptions, it is generally true. It is seldom that two solid bodies act chemically on each other, while fluids having mutual affinities, combine with facility ; and fluids act on solids with energy, proportioned to the attractions they have towards them. The fluidity in general necessary to chemical action, is communicated sometimes by the application of heat, sometimes by the addition of a fluid, which may dissolve or render fluid one or both of the bodies concerned, without materially altering the order of their attractions. Hence fusion and previous solution are the common *media* of chemical action.

It is not true, however, that fluidity is indispensable to chemical action. On the contrary, we have a number of examples in which two solid bodies in a state of minute mechanical division, act chemically on each other. We have such examples in several of the compound salts which decompose each other ; different solid salts too act on ice or snow at low temperatures, at which neither of them separately can be fluid, and various earths, when mixed together, and exposed to heat, combine and form a fusible compound, at a temperature much inferior to what would be requisite to communicate fluidity to either of them. In such cases, the mutual affinity is sufficiently strong to overcome the aggregation in each, and they establish the propriety of the expression of the general fact, that the at-

traction of aggregation in bodies, requires to be diminished below the force of the chemical attraction subsisting between them, in order that they may act on each other.

When the affinity of any fluid to a solid, has overcome the cohesion of the solid, and dissolved as large a portion of it as it can do, it may still dissolve a quantity of a different solid, by the affinity it exerts towards it; and it sometimes happens, from the reciprocal action of the two solids, that the solution of the second is effected in larger quantity, than it would have been if the other had not been previously dissolved. And if even a fresh portion of the first be added, it will now be dissolved. This was observed by Lemery in the solution of nitre and sea-salt in water. Vauquelin has found, that the same phenomenon is exhibited by a number of other saline substances *. Hence the reason that mixtures, of those salts which produce cold during their solution in water, produce it to a greater extent than when they are dissolved separately, as a larger quantity of solid matter becomes fluid in a shorter time; and hence also the difficulty found in many cases of separating completely salts by crystallization from the same solution, and the formation of an uncrystallizable residue †.

Cohesion, though much weakened in fluids, is not to be regarded as being totally impaired; its existence is

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* *Annales de Chimie*, t. xiii. 86.

† Berthollet's Researches, 163.

evident in the adhesion of the parts of a fluid forming globules, and it is still sufficiently powerful to resist even the reciprocal action, or to limit the combination of fluids the mutual affinities of which are weak. In general, however, the resistance it opposes is too inconsiderable to limit the combination, and hence fluids usually combine in all proportions, especially where the cohesion, such as it is, is not favoured by a considerable difference in specific gravity.

So far the operation of aggregation on chemical action was known to chemists. But besides the effects of it hitherto described, a more extensive influence has been attributed to it by Berthollet; and, considered under the point of view which he has pointed out, it is one of the most important of the causes concurring in the production and regulation of chemical action.

The principal peculiarity in the additional view which Berthollet gives of the influence of cohesion on chemical action, is, that he does not regard it merely as a quality of bodies actually solid, (or remaining in a small degree in fluids), resisting the efficacious exertion of affinity, and ceasing to act when solidity is destroyed: On the contrary, he conceives it still to operate when it has been apparently overcome, or when its effects are not sensible; and that by a progression in its action, it may at length materially influence chemical combination. It may be overcome by a superior affinity, or by the agency of heat; and its energy may be so far subdued, as to appear entirely negative; but it still continues so far active, that if the forces by which it was weakened are again diminished, its action will be

exerted, even before solidity takes place, and will counteract affinity. Or if, in consequence of new affinities, combinations are produced, it will frequently determine the proportions in which these are formed. Being exerted between the integrant particles resulting from the combination, whenever its intensity is sufficient to counterbalance the affinity of the liquid in which these are formed, it will produce separations, under the form of crystallizations and precipitations of the substance thus formed, it will of course withdraw it in part from the sphere of action, and will oppose a resistance to any further exertion of chemical power, and by such an operation will actually determine the proportions of the combination. This is the most important effect of cohesion; and I shall immediately have to state its agency in this respect more fully, in considering the limits of chemical attraction.

III. Insolubility.—The insolubility of a substance in a fluid, which is the medium of chemical action, has an influence on that action somewhat similar to that of cohesion, and is indeed nothing but a modification of it in relation to the fluid in which it is exerted. If substances in the liquid state be made to act on each other, their action will meet with little foreign resistance, and will be in a great measure proportioned to their affinity and quantity. But if one of them be solid, and be farther insoluble in the fluid which is the medium of action, the insoluble matter must present comparatively few points of contact; it must be always withdrawn from the sphere of action;

and of course, if it be opposed to a combination, it can act with comparatively little energy. From the same cause, if it be a compound, and be acted on by any substance tending to combine with one of its principles, its insolubility must in some measure protect it, as abstracting it from the action of the decomposing substance.

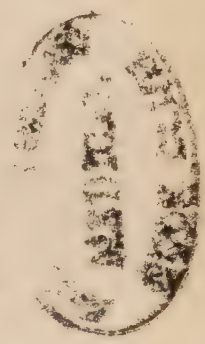
Insolubility may also determine the proportions in which a compound is formed; for if, in the progress of combination, a compound be produced which is insoluble, it will be immediately precipitated, become insulated, and thus fixed in its proportions.

Lastly, if an insoluble substance be the result of any chemical decomposition, by being immediately separated, it will not oppose the action of the decomposing substance, which it would have done if it had remained dissolved; and hence the decomposition will be more complete.

IV. Specific gravity.—Great specific gravity in a substance having much cohesion, or of sparing solubility, must co-operate with these qualities in influencing chemical action. It must withdraw the body possessed of it from the sphere of action, and the subsidence can be but imperfectly counteracted by agitation: hence it must in some measure retard its combinations; it must diminish its power in effecting decompositions; and it must, if the substance be a compound, oppose its decomposition from the action of other bodies upon it.

V. Elasticity.—This property is possessed in the highest degree, and indeed in such a degree only, as to produce sensible chemical effects by aëriform substances. Though the reverse of cohesion, it frequently operates on a similar principle, or influences chemical action, by withdrawing the particles from the sphere of attraction, and thus opposing or counteracting their combination. According to the different degrees of energy with which it is exerted, and according as it may be modified by other circumstances, it resists combination, or favours decomposition.

When two elastic fluids or airs are mixed together, having mutual affinities, in the greater number of cases they do not combine. *A priori*, we might perhaps be led to expect that they would combine with rapidity; for as cohesion is a force counteracting affinity, and as in the permanently elastic or aëriform fluids it is completely subverted, and a repulsion even established among the particles, any attraction existing between these particles, it might be supposed, would be exerted with full effect. We find this, however, very seldom the case; and between a number of elastic fluids, combination is slow and reluctant.



This is to be ascribed to their elasticity, and the distances at which their particles are placed. A substance existing in the aërial form, consists of a number of particles placed at great distances, and repelling each other. When two airs, therefore, are mingled together, their particles are without the sphere of chemical attraction; their mutual affinity is very

feebly exerted, and they cannot be combined, but by subjecting them to circumstances in which this obstacle is lessened or removed.

In conformity to this view of the operation of elasticity, in counteracting combination, it is found, that, in the elastic fluids the elasticity of which is not permanent, in other words, the vapours, the facility of combination is much greater than in the airs or gases; there is a strong tendency to condensation and approximation of their particles; they are on the verge as it were of fluidity: hence they are under circumstances favourable to their mutual action; they have no cohesion, and their elasticity is not permanent. When an affinity, therefore, exists between two bodies in the state of vapour, they often combine with facility. We find, even that when the affinity is very energetic in the permanent gases, it is capable of overcoming the obstacle from elasticity, and of uniting their particles, as in the example of the acid gases presented to ammonia. And even in those airs, which, when mixed together, do not enter into combination, an affinity appears to be so far exerted as to counteract their specific gravity, and prevent them from separating from each other. The mutual action is not sufficiently energetic to overcome the elasticity of each, and hence it is not attended by any change of volume, any evolution or absorption of heat, or the production of any new property, but is merely sufficient to retain them in a state of uniform diffusion. But if by any circumstances their elasticity is sufficiently diminished, their affinity is exerted with more energy,

and an intimate combination is formed. It has been found even, that by mechanical pressure, suddenly and forcibly applied, the particles of elastic fluids may be combined. Lastly, a combination may be more easily effected between a liquid and an air, than between two airs, since by the absence of elasticity in the one, while at the same time it has no great cohesion, the obstacle to the exertion of any attraction between them is much diminished, though it still continues to a certain extent, and limits the combination.

On the same principle is to be explained the effect of condensation, in promoting the combinations of elastic fluids. If an aëriform fluid be absorbed by water or any other liquid, the quantity absorbed will be much greater, if strong compression is applied, than if it is not; and by a compression sufficiently powerful, very large quantities of airs, which otherwise are very sparingly absorbed by the liquid, will be combined with it, and will remain combined as long as the compression is applied. The rationale of the operation is evident. The affinity of the aëriform fluid and the liquid, suppose it to be water, tends to combine them; the elasticity of the air opposes this combination; compression represses the elasticity, forces the particles nearer to each other, and of course nearer also to the surface of the water, and hence their mutual combination is effected. But if the compression is withdrawn, the temperature of the existing compound acts unequally on its component parts; the tendency of the air to elasticity is favoured, and the actual temperature may be sufficiently high to counteract the affini-

ty, and separate it from the water. These facts are equally observed in the absorption of those airs which have the strongest attraction to water.

Hence we find, too, that combinations of this kind are always promoted by cold. At a low temperature, more of the air is absorbed by the water than at a high temperature, because it is condensed by the cold, or its elasticity is repressed, while a high temperature, by augmenting the elasticity, causes its expulsion.

This, however, has its limits; for if the degree of cold be so great as to increase materially the cohesion of the fluid, this may more than counterbalance the advantage gained by the diminution of elasticity in the air, and may place bounds to the combination; and in freezing a fluid which has been previously combined with an air, it generally happens, from this cause, that in the moment of freezing the air is expelled. We find, too, that heat often favours the combination of aëriform fluids with solid substances; for although the application of heat increases the elasticity of the one, and so far is unfavourable to the combination, it diminishes the cohesion of the other, and this may so far exceed the opposite effect, as to enable the bodies to combine. In such cases, it generally happens, that by raising the heat still higher, the combination is again subverted, and the elastic ingredient expelled.

From these facts it follows, that elasticity is to be regarded as a force opposed to the combination of those substances possessed of it with other bodies, hether elastic or inelastic.

We have still to consider it under another point of view, as it favours decomposition.

If a compound consist of a solid substance, and of another, which, when pure, acquires elasticity, or exists in the aëriform state, such a compound will be more easy of decomposition, either by the application of heat, or by the intervention of superior affinity, than if it consisted of two inelastic bodies.

If it be exposed to heat, it will be unequally acted on; the elasticity of the one ingredient will be favoured; this elasticity will become more powerful, as the temperature is raised, and, at a certain point, will be able to counteract the affinity between the ingredients; they will be separated from each other, and the greater part of the one that is elastic expelled. A portion will indeed be retained, from the affinity of the solid base being increased, by the increase in its relative quantity by the progress of the decomposition; but this will be comparatively small.

The tendency to assume the elastic form, possessed by an ingredient of a compound, equally favours decomposition by a superior affinity, principally by withdrawing it from the sphere of chemical action. If, to a compound composed of an aëriform, and a solid or liquid body, a substance be added which has an attraction to the solid ingredient, it will of course combine with it, and exclude a portion of the air that was in combination. If this, however, were to remain within the sphere of action, it would oppose a resistance to the progress of the decomposition, and the solid ingredient would be shared between it and the de-

composing substance, in proportions determined by the respective energies of their affinities. But the aëriform body, as it is disengaged from its combination, passes into the elastic state, is withdrawn entirely from the sphere of action, and no resistance is opposed to the progress of the decomposition. Hence the decomposition of compounds of this kind;—those consisting of a solid or liquid substance combined with an air, are more complete than the decomposition of compounds, consisting of inelastic ingredients. Among the salts, this facility of decomposition is obvious in the carbonates, and in the muriates and fluates; though, in the two latter, to a less extent, from the stronger affinity their acids have to water, and perhaps also the greater energy of their attraction. Such decompositions also are much favoured by the application of heat, which, increasing the elasticity of the volatile substance, favours the affinity of the more fixed, and frequently causes it to predominate though in itself weaker than the affinity of the elastic ingredient to the base of the combination.

VI. Efflorescence.—The effect of this property on chemical action, is comparatively trivial and confined. Scheele had observed, that in several saline mixtures, made into the consistence of a paste, certain decompositions were produced, and that one of the compounds, resulting from the decomposition, rose gradually through the mass, and formed an efflorescence on its surface. Berthollet supposes, apparently with reason, that its being thus withdrawn from the sphere of action, will contribute to the progress of

the decomposition, or allow it to proceed farther than it would otherwise have done. The case in which it has been principally observed, is in the decomposition of common sea-salt by lime, or by iron, noticed by Scheele; and Berthollet applied the observation to the explanation of the production of mineral alkali or soda, in the beds of lakes in Egypt. It serves to explain the appearance of the same substance on walls covered with mortar, and perhaps it may be applied with advantage in practical chemistry. The circumstances which appear to favour it, are a porous mass, a certain degree of humidity, and a disposition to crystallize in the efflorescent substance.

VII. Temperature.—Much of the effect of temperature on chemical action, is to be ascribed to the operation of some of the preceding causes, and particularly to the changes which heat and cold produce on the cohesion and the elasticity of bodies. Its effect, however, is more frequently compounded of the two, or arises from the changes produced on the cohesion and elasticity at the same time. On this account, it requires a separate statement; and this also is demanded by the importance of the subject.

In general, the application of heat favours combination; or two bodies, which, at a low temperature, do not act on each other, combine when their temperature is raised; and with regard to many substances, it is necessary that it should be raised even to ignition, to effect their combination.

Where one or both of the bodies, whose combina-

tion is promoted by heat, are melted by its operation, it is easy to perceive to what cause its influence is to be ascribed; it must be to its overcoming the cohesion of the fused substance, and thus removing an obstacle to the exertion of affinity. But there are many cases in which, without fusing bodies, or producing any change on their forms, heat still favours their combination, as in the solutions of salts in water, the mutual action of earths, the combinations of metals and solid inflammables with oxygen, and many others. In these, it is still to be regarded as operating, by so far lessening the cohesion of the solid bodies. Every degree of heat communicated to a solid substance, weakens its cohesion, though it may not be capable of overcoming it to that extent, as to cause it to pass into the fluid form; and this diminution of cohesion, may so far remove the obstacle to combination, that if a powerful affinity exist between the bodies, it may be exerted with effect.

The power of heat, however, in thus favouring combination, by diminishing cohesion, is frequently counteracted by its increasing at the same time elasticity. If an elastic fluid is to be combined with a solid, the obstacles to the exertion of their mutual attraction, are the cohesion of the one and the elasticity of the other. Heat will diminish the former, but it will also augment the latter; and so far as the one effect would favour combination, the other will oppose it. Hence, if the affinity existing between these substances is not strong, it may not be possible to effect their combination, by raising their temperature, as is the

case, for example, in exposing gold or silver to oxygen gas. Or if at one degree of temperature they have combined together, the exposing the compound to a still higher temperature, may again separate them, as is the case with quicksilver and oxygen. Hence also, if the cohesion is lessened by other means, the combination may be effected at a moderate temperature, as we observe in the facility with which metallic alloys, and especially alloys of the metals with quicksilver combine with oxygen, compared with the same metals in their pure state. Their cohesion is so far lessened in these combinations, that a moderate heat is sufficient to diminish it to that degree, that even with the augmentation of elasticity in the oxygen gas, which the heat causes at the same time, the resistance to the exertion of attraction is on the whole lessened, and the substances combine.

Even the same operation, to a certain extent, may influence the mutual action of inelastic substances. If the action of a fluid on a solid be aided by heat, the whole effect arising from the diminution of cohesion in the solid may not be obtained, as it may partly be counteracted, from the expansion produced at the same time in the fluid, and if the fluid be highly expansible or volatile, this may considerably weaken the energy of its affinity.

To the operation of heat on cohesion and elasticity, now described, are to be attributed the differences of affinity between the same substance, when exerted in the humid way or by the medium of solution, and in the dry way or by exposure to heat. In the former,

cohesion is counteracted, while the elasticity of any of the ingredients is not affected; in the latter, if the one power is diminished, the other is augmented, and this is frequently sufficient to change the results. Bergman pointed out this operation of heat on elasticity, as modifying the affinities exerted under these different circumstances *.

A high temperature, or the application of heat, is equally powerful in favouring chemical decomposition. Many substances remain in union within a considerable range of temperature; but if the temperature be raised beyond a certain point, the attraction by which they were united is weakened, they separate, and the compound is decomposed. Such decompositions from a high temperature take place generally, perhaps always, in those compounds, one of the ingredients of which exists when uncombined in the aëriform state. Hence, the operation of heat in occasioning them is evidently owing to its favouring the elasticity of this ingredient, acting on it with greater effect than on the other, and by the distance at which it places the particles overcoming their mutual attraction.

In some cases of decomposition favoured by heat, the attraction of a third body is introduced; but the explanation of the agency of the high temperature is still the same. By adding to the elasticity of the more volatile ingredient, it weakens its affinity, and hence favours the combination of the two substances which

* Dissertation on Elective Attractions, p. 15.

are more fixed. From this it is evident, that it cannot be inferred, from such decompositions, that the affinity of the decomposing substance has been superior to the affinity of the substance which, with the aid of heat, it has expelled from the combination.

On the same principle, heat often favours the mutual decomposition of two compounds mixed together, favouring the union of the two more volatile ingredients, and thus allowing an attraction to be exerted with less resistance between the two which are comparatively fixed.

In all cases, therefore, in which heat favours chemical action, it does so by the change it occasions in the cohesion or in the elasticity of the bodies concerned; but the one of these often modifies the effect which would result from the other, and thus this power, in many cases, apparently produces opposite effects. In a certain degree it will favour combination, and in a still higher degree it will occasion the decomposition of the very substances it had enabled to combine; and it is only by considering these in combination, that we obtain a just theory of its operation.

The same view is to be taken of the operation of a low temperature or of cold on chemical action. By diminishing elasticity, it frequently favours combinations; and in other cases, by increasing cohesion, it may determine combinations, or may subvert existing affinities, and give rise to decompositions. And in the same case, it may happen, that both qualities may be affected, and may produce results, which, if this were not attended to, would not be expected. By a low

temperature, we may thus promote the combination of an aëriform body with a liquid; but if we reduce the temperature too low, that is, near to the point at which the liquid congeals, the additional force given to cohesion may counteract the effect arising from the diminution of elasticity, and may impede the combination. Or if the temperature be reduced so low as actually to freeze the fluid, an aëriform body held in solution by it may be expelled, owing to the cohesion acquired by the congelation.

The circumstances now enumerated, not only influence the exertion of chemical attraction as to its force, but also as to its rapidity. Where the cohesion of a body is great, it will be more slowly acted on by a fluid than if the cohesion were less considerable: hence the utility of those operations which diminish aggregation, in promoting chemical action. It is obvious, also, that chemical action must be slower when resulting from a weak than when arising from an energetic attraction; and, for the same reason, as the force of attraction diminishes as bodies approach to saturation, a chemical action which at its commencement may be rapid and violent, must in its progress become more slow. Agitation hastens the chemical action of a solid or a liquid, by removing from the surface of the solid the portion of the liquid already saturated with it, and which, from its greater specific gravity, would otherwise remain covering it, and protecting it from the action of the rest of the liquid. And, on a similar principle, agitation accelerates the combination of an aëriform body with a li-

quid, renewing the surface, and distributing with uniformity the combination over the whole mass. Lastly, a high temperature renders chemical action more rapid, by diminishing or removing those circumstances by which affinity is counteracted.

It is often neceſſary to attend to the slowness of chemical action to avoid erroneous conclusions; substances, which, when mixed together, give no indication of mutual action, acting and producing even complete changes when sufficient time is allowed.

From the important influence of the circumstances by which chemical attraction is counteracted, it is obvious, that we cannot infer, with regard to any two bodies, that they have no mutual attraction; since, although they cannot be combined, this may arise, not from the absence of attraction, but from the influence of one or other of the circumstances by which that power is modified, and which may entirely predominate over a weak affinity. The principle is even probable, *a priori*, that attractions exist between the particles of every kind of matter. Note (A c).

Sect. IV. *Of the Modification of Affinities resulting from Combination.*

From the influence of the forces enumerated in the preceding section, on the exertion of chemical affinity, combined with the conclusion that all bodies have attractions to each other, it follows as a very probable

conclusion, that the affinities exerted by compounds may be merely the affinities of their constituent principles, modified by the conditions in which they exist in the compound. The affinities of the compound are often, indeed, extremely different from those of its elements; but, when the important influence of saturation, of cohesion, and of elasticity, are considered, these circumstances will perhaps be found sufficient to account for such differences, by the changes they necessarily must produce in the elementary affinities.

The subject has accordingly been considered under this point of view by Berthollet, and he has pointed out these circumstances, as modifying, in a combination, the affinities of its elements.

Thus, it is obvious, that the action of substances diminishing in proportion to their saturation, the affinities of a compound must, from this cause, be in general less strong than those of its constituent parts. Other circumstances may at the same time either counterbalance this, and render the affinities actually more energetic, or on the other hand may concur with saturation in diminishing their force.

Thus, if one of the substances combining, pass from the solid to the liquid state, it acquires the advantages derived from liquidity, and its affinities, formerly counteracted by its cohesion, may now, notwithstanding its combination, be exerted with more effect. Or, if elastic substances, by combination, form a liquid compound, the advantage gained by this condensation and removal of elasticity, may more than counterbalance the diminution of force from combination, and

may thus render their affinities both more powerful and more extensive in their action.

On the other hand, if the result of a combination is the transition of a substance into the concrete state, the cohesion thus acquired will concur with the saturation in diminishing the energy of its action; as may also its transition from the liquid to the gaseous form.

We thus perceive how, supposing the affinities of substances to remain in their combinations, they may still be altogether different from what they were in the simple elements. Berthollet has stated a number of facts from the details of chemistry, which accord extremely well with these views, and of which a few are mentioned, Note (A d).

The action which proceeds from several affinities in the same substance, thus balanced, is termed by Berthollet RESULTING AFFINITY, in opposition to the individual affinities belonging to the principles of a compound, which he names ELEMENTARY. The affinities exerted by water, which is a compound substance, may be named resulting, though the elementary affinities of its constituent principles may also be sometimes separately exerted. As chemical action is reciprocal, the name of Resulting Affinity is likewise given by this chemist to the attraction which a simple substance exerts to a compound when it does not change the composition of the compound. Thus, a substance exerting an attraction to one of the principles of water, exerts an elementary affinity; when it exerts attractions to both, in other words, to the compound itself, the affinity is resulting.

At the same time, these modified affinities in a compound, though they may be traced from those of its constituent parts, should still be regarded as a single and integral force, operating as such while the body remains undecomposed; and we may speak with equal propriety of the affinity of a compound, as of the affinity of a simple substance.

The question now stated is not merely a theoretical one, but leads to some important results. It in particular enables us to explain some anomalous cases of chemical action; those which have been classed under what is named Disposing Affinity, and which appear to arise principally from the modifications produced in elementary affinities by combination.

The actions which have been thus classed together, are of a very peculiar kind. In a number of cases, two bodies are found incapable, under given circumstances, of combining together; but the circumstances still remaining the same, their combination is effected by the addition of a third body, though it has no apparent attraction to either of the others; or at least none which, by any obvious operation, can facilitate their union. It has been observed, indeed, that the substance which thus predisposes to the combination, or exerts the disposing affinity, has an attraction to the compound which is formed by the combination of the others, and to this attraction its agency has very absurdly been ascribed, since the attraction which it might exert to a substance if it were formed, cannot be a cause of the formation of that substance.

Sulphur is incapable, at any natural temperature,

of combining with oxygen; but if it be combined with lime, and the compound dissolved in water, it attracts oxygen with facility. The lime, therefore, is said to exert a disposing affinity. The *rationale* of this case appears to be, that the sulphur, by this combination with lime, and its solution, loses its cohesion, and thus one obstacle is removed to its union with the oxygen, without the elasticity of that oxygen being increased, which it would be, were the sulphur rendered fluid by heat. At the same time, its combination with that principle will be favoured by the affinity of the lime to the oxygen, which, though feeble, still exists; or a resulting affinity, which the circumstances of this combination render more powerful than the elementary affinities, is established, the tendency of which is to unite the sulphur, oxygen, and lime, and accordingly this combination is effected.

Water is a compound of oxygen and hydrogen. Iron has an affinity to oxygen; but, under the circumstances which exist, not sufficient to decompose water with any sensible celerity at a common temperature. But, if a little sulphuric acid be added, the decomposition of the water by the iron commences, and proceeds rapidly, the iron receives oxygen, and the compound thus formed combines with the acid. In this case also the acid is said to operate by a disposing affinity. Its agency is ascribed by Berthollet, to the tendency it has to combine with the iron, and with a portion of oxygen, which, co-operating with the attraction of the iron also to the oxygen, these concurrent affinities

cause the decomposition of the water; and a combination of the acid, the iron, and the oxygen abstracted from the water, is formed.

"All the effects of affinity which have been termed "*Predisposing*, may be ascribed to this union of forces."

SECT. V. *On the Limits to the Exertion of Chemical Attraction.*

THE attraction exerted from one body to another, may be limited to certain proportions, in which only they are disposed to combine; and the attractions of any individual to others, may be limited as to the number of substances with which it can enter into simultaneous combinations. These form two subjects, distinct from each other, but both comprized under the subject of the present section—the limits observed in the exertion of chemical attraction.

I. In the greater number of chemical combinations, there are limits to the attraction which is exerted, with regard to proportion or quantity, or the substances are not in general capable of combining in indefinite quantities, but can be united only in precise or determinate proportions.

Under this proposition, which has been stated even as a law of chemical attraction, I have formerly arranged the following varieties of the general fact.

In the *first* place, there are many bodies which have a strong mutual attraction, but which exert it with ef-

fect in such a manner as invariably to unite them in one determinate portion; nor is it possible to combine them in any other, in whatever quantities we present them to each other. If an excess of either, above the precise proportion be present, it remains uncombined, and of course with its properties unimpaired. The constituent principles of water afford an illustration of this variety of combination, and it is exemplified in several others.

2*dly*, There are cases in which bodies combine in more than one determinate proportion, in two, three, or perhaps four; but in the proportions intermediate between these, no combination can be effected. The constituent principles of our atmosphere, oxygen and nitrogen, afford an example of this variety of combination. When brought into intimate combination, they exert a mutual attraction in at least three determinate proportions; 37 of oxygen may be combined with 63 of nitrogen, forming one compound; 56 of oxygen may be combined with 44 of nitrogen, forming another compound; and there can be effected still another combination of these principles, in the proportion of 70.5 with 29.5. But these two bodies cannot be combined in any other quantities than these; and if presented to each other in different proportions, and placed under the circumstances favourable to their union, it will always take place in one of these determinate quantities. The same law is observed in the combinations of many other substances.

The compounds formed by these combinations of the same principles in different proportions, differ always in their properties from each other, and frequent-

ly the differences are as great as between compounds formed of principles perfectly dissimilar. Nearly all the varieties of properties among the substances belonging either to the vegetable or animal kingdom, are to be ascribed principally to this cause. They consist of the same principles, and derive their distinctive properties chiefly from the proportions in which these are combined.

There is a *third* variety of the exertion of chemical attraction, that in which it is unlimited to a certain extent, beyond which the power of combination ceases. This is illustrated by the solution of a salt in water. Here determinate proportions, and a succession of compounds, are not observed. Any quantity of the salt, up to a certain proportion, may be combined with the water; but if we proceed adding more and more salt, we at length arrive at a point beyond which we cannot proceed; attraction is no longer exerted, and any quantity of salt that may be added remains undissolved.

Lastly, There are cases of combination absolutely unlimited, or in which bodies will combine together, in whatever proportion they are presented to each other. This is observed principally in the combinations of fluids with each other, where the result of the combination is a substance still existing in the fluid form, as in the example of alkohol and water.

When combination takes place in different proportions, it often happens, that, in a certain proportion, the properties of the bodies are mutually neutralized, or the compound retains the more distinctive proper-

ties of neither of its component parts; while in other proportions, where there is an excess of either ingredient, its properties may be recognized, weakened perhaps, but still to a certain degree energetic in the compound. The proportion in which the properties are mutually lost, is termed that of *Saturation*, and the two substances are said to be mutually saturated or neutralized. The term saturation has also been understood in another sense; or it has been used to denote that extreme of combination in which a body is combined with the largest proportion of another; as, when water has dissolved the largest proportion of salt which it can do, it is said to be saturated. These two points, that of the neutralization of properties, and that of the extreme of combination, seldom coincide. It would be better to apply the term neutralization to the former, and restrict that of saturation to the latter.

Such are the different classes of facts to be arranged under the general proposition. There are some bodies which can be combined together in only one proportion; there are others which may be combined in two, three or four determinate proportions; some have a power of combination, unlimited to a certain extent, beyond which the capability of combination ceases; and lastly, there are a number of bodies between which combination takes place in every possible proportion.

It were desirable to reduce, if possible, these varieties of combination to some general principle. On this subject, however, scarcely any theory has been

proposed. When substances combined in determinate proportions, it was considered merely as an attribute of chemical affinity thus to limit proportions; nor was it attempted to be explained, why this limitation should be effected in such various modes, or why, in some cases, it did not take place. Berthollet has endeavoured to solve this problem, and to point out the causes on which the limitation of affinity with regard to proportion depends.

The principle on which he proceeds is, that chemical action being exerted in the ratio of the affinity of the substances concerned, and of their quantities, there is no point at which it ceases to operate; that, in all cases, therefore, bodies are disposed to combine without limitation, or in every possible proportion; and limits are placed to the combination, or determinate proportions established only by the interference of foreign forces, cohesion, elasticity, or some other of those circumstances, which, it has been shewn, so powerfully modify chemical action.

Where circumstances of this kind do not interfere with much force, as in the mutual action of two liquids, the result of which is a substance still existing in the liquid state, combination in general takes place in every proportion. When cohesion or elasticity is present in the subjects of the combination, as in the action of a liquid on a solid, or in the absorption of an aëriform substance by a liquid, these forces limit the quantity of the solid that can be dissolved, or of the air that is absorbed, in the manner already explained; the affinity producing the combination, diminishing in force as the

combination proceeds, while the cohesion of the remaining solid, or the elasticity of the unabsorbed air, continues as at first, an equilibrium must necessarily be arrived at, when the combination will cease. Up to that period, therefore, it may take place in indeterminate proportions; but when it is reached, a limit is placed, beyond which it cannot proceed. Lastly, When in the progress of combination, the result in any part of it is great condensation; this, by the obstacle it may oppose to the exertion of affinity, or even from the greatness of the condensation, by withdrawing the product from the sphere of action, may limit the combination to that point, or to the proportion at which this effect is greatest; or if, by particular circumstances, this is overcome, in the further progress of the combination, it may again happen; and, in this way, compounds, in two or three determinate proportions, may be formed. The further illustration of these explanations may be introduced with more propriety in a note. Note (A e).

II. The attractions of any body towards others, may be limited as to the number with which it can enter into simultaneous combination.

I have hitherto spoken of chemical attraction, as exerted between two bodies. It may be exerted, however, between more than two, or may bring three or four substances into one combination.

If three substances are placed within the sphere of chemical action, it generally happens, either that two of them combine, to the exclusion of the third, or that one is combined with each of the others, being divided

between them in proportions determined by their affinities and quantities; and thus two distinct compounds are formed. In some cases, however, instead of either of these varieties of combination, the three substances have their affinities mutually balanced, in such a manner that they enter into simultaneous combination, and form only one compound. Even four, five, or perhaps more substances, may be thus combined together. Such combinations are named Ternary, Quaternary, &c. according to the number of their constituent parts.

We have numerous examples of such combinations among the metals. If three or four metals be fused together, they often unite, and form one uniform compound. We have also frequent examples of ternary combinations among the salts, one acid being saturated by the joint action of two bases.

Nature, too, presents us with a number of such combinations. Nearly all the substances belonging to the vegetable kingdom are compounds of at least three principles; and the composition of the animal products is still more complicated, four or five principles being combined in their formation.

These combinations appear to take place principally among bodies in which the mutual attractions, under given circumstances, are nearly of the same force, and where the binary compounds they would form, do not differ much from each other in cohesion, or the other qualities which determine combination. Did the attraction of one ingredient to any of the others much exceed their mutual affinities, it would probably give rise to an insulated binary compound; or did the compound re-

sulting from the union of any two of the ingredients, differ much in its constitution from those formed by the others, this circumstance would determine the chemical action, and cause the separation of such a compound. But where neither of these circumstances is present, the affinities may be balanced, and give rise to one combination. Hence, probably, their formation more peculiarly in the vessels of vegetables and animals, where, from the constant motion and agitation to which they are subjected, the compression under which they are placed, and the smallness of the mass in which the affinities operate, the circumstances of cohesion and elasticity are in a great measure prevented from operating, and giving rise, as they otherwise would do, to binary combinations. It appears to follow, indeed, from the speculations of Berthollet, that in all cases where substances may be mixed together, in whatever number, the tendency is, to form an individual combination, in which the forces will be reciprocally balanced; and that binary combinations are determined only by the interference of cohesion, elasticity, or the other external forces by which chemical action is modified.

SECT. VI. *Of the Forces with which Chemical Attraction is exerted.*

ALL the phenomena of chemistry concur in proving, that different bodies exert very different forces of affinity; and could these forces be accurately determined,

the science might rest on the basis of calculation. The subject of the present section is therefore highly interesting, though it is also considerably complicated and obscure.

It is first necessary to explain the doctrines of Single and Double Elective Attraction, the phenomena of which have usually been referred to the relative forces of affinity exerted among bodies. In consequence of the attractions which one body has to others, numerous series of combinations may be formed; but, from its attractions differing in force, these combinations, it has been supposed, can be subverted, and the compounds formed decomposed.

Suppose A have to B a force of affinity, which, under given circumstances, may be said to be equal to 6. If presented to each other, and there be no effectual obstacle to the exertion of this attraction, they will enter into combination, and form the compound A B. But suppose C, a third body, have an attraction to A, which, under the same circumstances, is equal to 8, when C is presented to the compound A B, it will decompose it, A and C will unite, and form a new compound, and B will be separated in an uncombined state. A decomposition, it is evident, would also have equally taken place, if C, instead of exerting a superior attraction to A, had exerted it to B, these two would have combined, and A would have been separated.

This forms what the chemists have been accustomed to term Single Elective Attraction. Every substance has attractions towards others, and is, therefore, capable of combining with them. But it does not ex-

ert the tendency to combination with the same force to all; on the contrary, this tendency is greater, as exerted to some than to others, and to each it is different in its degree. If, therefore, the body be combined with one to which it has comparatively a weak affinity, the compound which is formed will be decomposed, by the addition of any body to which it has a stronger attraction; the two combining, between which the attraction is strongest, and excluding the other. Hence arise an extensive series of decompositions, and hence is derived the power which the chemist has of recovering the substances he has combined together, and of obtaining also the simple elements of which the products of nature are formed. It is to be carefully attended to, however, as a matter of fact, that in these cases of single elective attraction, there is generally a partition of action, whence the decompositions are not complete. When the compound A B is decomposed, by C exerting an attraction to A, in proportion as A is abstracted by C, the affinity of B to A is increased by its quantity, and hence it retains a portion of it still combined; and it is only in cases where the agency of C is strongly favoured by the circumstances influencing chemical action, that a complete decomposition of A B will be obtained. Frequently, too, the ingredient of a compound which is excluded, attracts a portion of the decomposing substance, and is from this cause not obtained pure.

When this difference in the relative forces of attraction was observed, it was a very obvious idea to construct tables in which they might be represented, as

far as they were ascertained by experiment. This was first done by Geoffroy, a French chemist, in 1718, and since his time the labours of many chemists have been directed towards correcting and extending these tables. Their construction is extremely simple. The substance whose attractions are to be enumerated, is placed at the head of a column, and the different substances to which it has an attraction, are placed beneath it, in the order of the forces of attraction, the substance to which it has the strongest attraction being immediately under it, the others following in that order, and the one to which it has the weakest attraction of course closing the column. Thus the attractions of lime and of muriatic acid, are represented in the following table, to the substances inserted in them.

Lime.	Muriatic acid.
Oxalic acid.	Barytes.
Sulphuric acid.	Potassa.
Tartarous acid.	Soda.
Phosphoric acid.	Lime.
Nitric acid.	Ammonia.
Muriatic acid.	Magnesia.

Bergman undertook the task of extending and correcting the tables of single elective attraction, which had before been constructed; and since his time some additions have been made to them. Though their utility may now be questioned, at least in their full extent, yet as expressing the order of decomposition under given circumstances, in many cases of chemical ac-

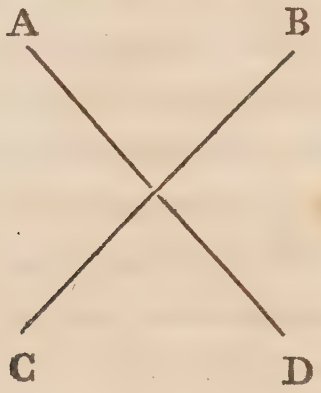
tion, I shall, so far as they have been ascertained with accuracy, insert them under the history of the substances to which they refer.

I have now to explain a case of elective attraction, more complicated.

Suppose we have a compound, formed by the union of A and B, in which the force of attraction is equal to 20, and that to this compound another substance, C, is added, which has an attraction to A, equal to 16, it is evident that no decomposition can ensue. But suppose, a fourth substance D, is united to C, with an attraction equal to 7, and suppose that D has an attraction to B equal to 12, then a decomposition must be effected on mixing these two compounds; for the sum of their existing attractions is inferior to the sum of those tending to separate them, the former, the affinity of A to B and the affinity of C to D, being equal only to 27, the latter, the affinity of C to A and of D to B, being equal to 28. A B, C D, therefore are decomposed, and two new compounds, C A, B D, are formed.

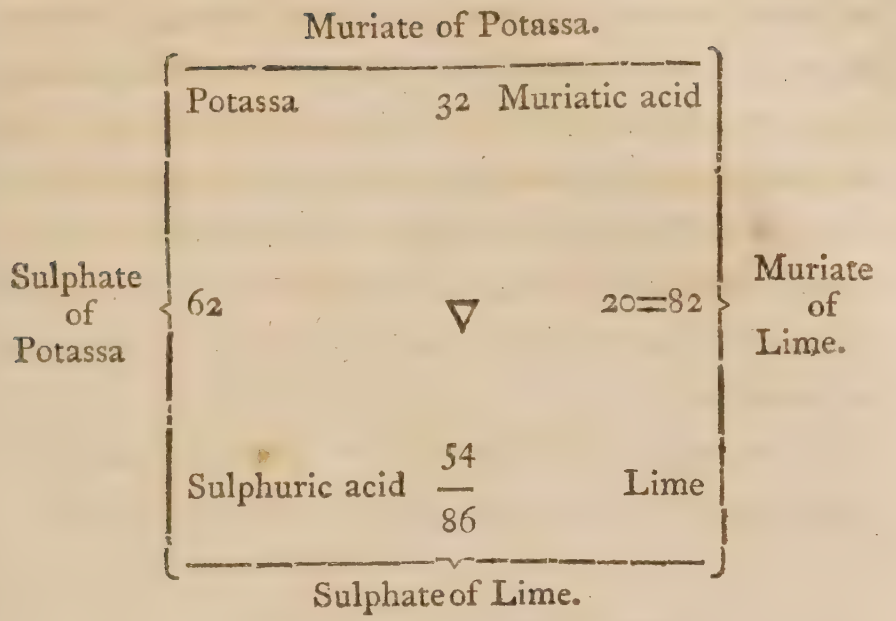
This is what is termed, in the language of chemistry, Double Elective Attraction; two elective attractions being exerted, and two new compounds formed. Of the two attractions which are exerted, the tendency of the one is to preserve the original compounds undecomposed, that of the other is to separate their principles. The former have been termed by Mr Kirwan, the Quiescent, the latter, the Divellent Attractions, terms which are generally used. It is evident, that a double decomposition can only be effected, where the sum of the divellent is superior to that of the quiescent attractions.

In order to represent more clearly and concisely what passes in these complicated attractions, diagrams have been constructed. The idea seems first to have occured to Dr Cullen. The one he proposed was, that of two cylinders crossing each other at the middle.



If on mixing the compounds denoted by A C, B D, the attractions of A to B, and of C to D, overcome the quiescent attractions, A C, B D; the resulting decomposition is represented, by supposing the extremities A B, C D, of the cylinders to be brought together; by which also the production of the two new compounds will be denoted by the conjunction of these letters.

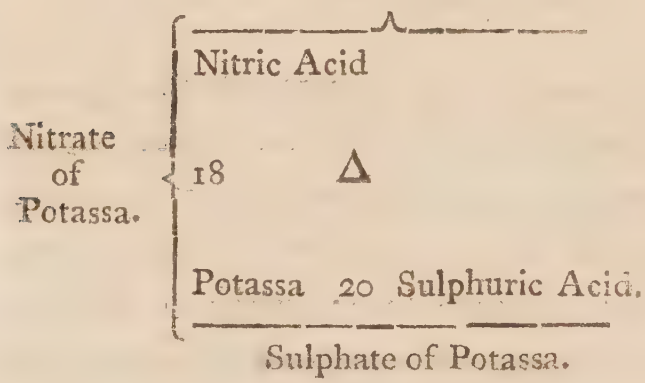
The diagram proposed by Bergman, consists of two brackets connected by straight lines, forming a square, at the sides and corners of which, the names of the existing compounds, and of their ingredients, are placed; and though not conveying a more clear idea of the operation itself, is better calculated to represent all the circumstances connected with it.



Thus in the scheme which Bergman himself gives, if the two compounds, termed Sulphate of Potassa, and Muriate of Lime, the former consisting of sulphuric acid and potassa, the latter of muriatic acid and lime, be mixed together, a double decomposition takes place, and two new compounds, muriate of potassa, and sulphate of lime, are formed. This is represented by placing on the outer sides of the two brackets the names of the two compounds mixed, and at the corners of the brackets, the names of their ingredients, so disposed that the one acid shall be diagonally opposite to the other. If the numbers expressing the relative force of attractions of the principles of these compounds be also added, it will be obvious that a decomposition will ensue. If the attraction between potassa and sulphuric acid be 62, and that between lime and muriatic acid 20, the sum of the quiescent attractions will be 82. But if

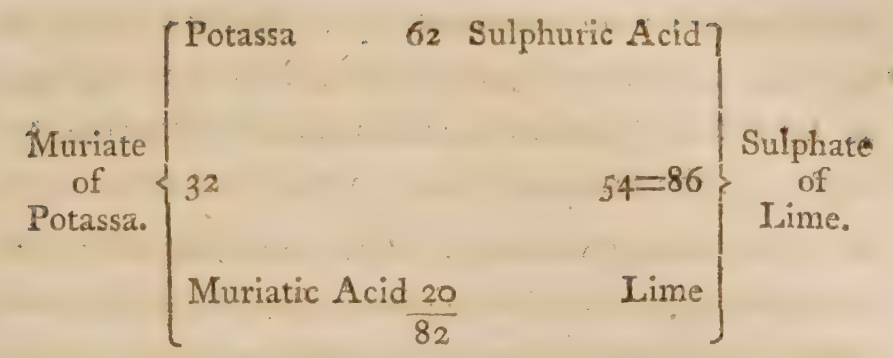
the attraction between potassa and muriatic acid be 32, and that between sulphuric acid and lime 54, the sum of the divellent attractions will be 86. These, therefore, will operate with effect; the muriatic acid and the potassa will combine together, as will the sulphuric acid and the lime, and the names of these resulting compounds, muriate of potassa and sulphate of lime, are placed without the straight lines, by which the brackets are connected.

To represent a single elective attraction, the same figure is used, with one bracket, as in this diagram.



By some slight variations in their construction, these diagrams have been rendered still more extensive, so that they are capable of representing all the phenomena of these combinations.

Where the quiescent attractions are superior to the divellent, and where of course no decomposition takes place, the scheme consists of two unconnected brackets, with the names of the compounds at each side, and of their ingredients at each corner; the numbers, denoting the forces of attraction, being interposed.



In the opposite case, where decomposition is effected, the schemes No. 2. and No. 3. are used, varied only to shew the peculiar phenomena.

Thus, in such decompositions it frequently happens, that one or both of the new compounds prove insoluble, and consequently fall down. This is denoted by bending downwards, in the middle, the line placed between the substance and the square, as in diagram 2. where the undermost line is bent down to shew that the Sulphate of Lime is precipitated. If, on the contrary, one of the substances be volatilized or sublimed, the line is bent upwards in the middle, as in diagram 3., where the upper line is drawn in this manner, to shew that the Nitric Acid is volatilized. If they are neither precipitated nor volatilized, the brackets are merely connected by two straight lines.

Lastly, the circumstances under which the decomposition takes place, require to be pointed out. Sometimes it is effected by the substances being dissolved by water, sometimes by the application of heat to them in the solid state. Bergman distinguished these decompositions in the humid and in the dry way, by inserting in the middle of the diagram a triangle, Δ,

which was the old chemical mark for fire, to denote that the decomposition was effected in the dry way, or by the application of heat; and an inverted triangle, ▽, the mark for water to point out when it was done in a watery solution. The same method is still used, the signs only having been changed, a perpendicular line | being the mark for caloric or heat, and the compound figure, ⨪, for water. To facilitate the construction of such diagrams, all the chemical agents have likewise been distinguished by particular signs or characters.

A number of cases of compound affinity have been given by Bergman under the form of his diagram. These have been corrected and enlarged by Dr Pearson in a separate work.

I have thus stated the doctrines of single and double elective attraction, as they were delivered by Bergman, and until lately universally received by chemists. I have now to add, that a different view has been given by Berthollet of these changes, deduced from experiment, and undoubtedly according with many chemical facts.

In Bergman's theory, affinity is regarded as an invariable force; and all the decompositions which were ascribed to elective attraction, are considered as depending on the various degrees of intensity with which that attraction is exerted by each body towards others. The results have been considered as capable of measuring even the relative forces of affinity, and of course as arising solely from them.

In the theory of Berthollet, the changes ascribed by

Bergman to the predominance of certain affinities over others, are referred to the operation of those circumstances by which attraction is influenced, and combination limited.

If the substances which in any case of complex affinity act on each other be liquid, or be soluble in the fluid, which is the medium of action, and if the compounds they form in any stage of combination have no great cohesion or insolubility, no evident change appears when they are mixed together, there is a mutual saturation, and the opposing substances remain united, forming an individual combination, in which the forces are balanced. But if, on any of the parts of such a combination, the force of cohesion or insolubility, or the power of elasticity operate with energy, these external forces will subvert the balance, will give rise to separations, and will hence be the real cause of the results which in the old theory were ascribed to the predominance of divellent over quiescent affinities.

Thus, if four substances are presented to each other, two of which have a greater tendency to cohesion than the others, or which form a compound of sparing solubility, and the other two a compound of a different nature; instead of the four forming one combination, in which the affinities are balanced, this combination will be counteracted by the force of cohesion, and the two which form the insoluble compound will combine together, and be separated by precipitation or crystallization, the other two remaining in combination in the fluid which has been the medium of action.

If even these four substances were previously in the reverse binary combinations, on presenting them to each other, the affinities within the sphere of action must be reciprocally exerted; and the same extraneous forces will cause an exchange of principles, or the phenomena which have been ascribed to elective affinities will be produced. In other words, if A and B when united form an insoluble compound, and C D one that is soluble, if A has been previously combined with C, and B with D, on mixing these two compounds, the result will not be reciprocal saturation and a simultaneous combination, but the force of cohesion operating with more energy on the combination of A and B, it will separate, while the other two ingredients, C and D, will remain in union. Cases of this kind he denominates Complex Affinity, to avoid the term Elective Attraction, which in some measure implies an hypothesis.

The case will be the same with regard to a single elective attraction, or where three substances are presented to each other. If the combination of two of them give rise to a substance of sparing solubility, or having a strong tendency to cohesion, this circumstance will determine their union, and the separation of the insoluble compound, instead of the balance of affinities of all the three substances which would otherwise have been the result

Hence, "if all the decompositions ascribed to com-
"plex affinities be investigated, it will be found, that
"the prevailing affinity has been always ascribed to
"those substances which have the property of pre-

"cipitating, or of forming a salt which can be sepa-
"rated by crystallization. For this reason, it may
"be inferred *a priori*, from a knowledge of the solu-
"bility of salts, which may be formed in a liquid,
"that those substances which are least soluble, and
"most apt therefore to precipitate, will be found to
"be the same as those to which Bergman and other
"learned chemists have attributed the strongest af-
"finity in their tables *."

These combinations are at the same time considerably influenced by the proportions of the substances presented to each other. The exchange of principles is scarcely ever complete; and Berthollet, by a number of experiments on the compound salts, has shewn that the products from their mutual action are different, according to the relative proportions in which they have been mixed together, especially where the force of cohesion has not been exerted with much energy, so as to render imperceptible the effect of quantity †. Where this force is considerable, and unequal in the combinations which take place, it determines the exchange of bases, and the precipitation of the insoluble compound, independent of proportions. But where it is less energetic, the influence of quantity may be traced, and hence the formation of salts obtained by slow crystallization depends much on the proportions of the substances acting on each other: in such cases, as Berthollet has re-

* Researches into the Laws of Chemical Affinity, p. 106.

† Researches, p. 156.

marked, "a succession of different combinations takes "place, according to the forces which predominate at "the moment at which the separation commences."

Other decompositions, particularly those where the application of heat is necessary, are occasioned by the operation of elasticity.

If one of the ingredients of a compound, have a tendency to assume the elastic form,—when such a compound is acted on by a substance capable of combining with its other ingredient or base, if its decomposition be effected, we are not to ascribe it, with Bergman, to the predominance of a powerful affinity over one more weak: it is owing to the tendency of the elastic ingredient to escape from its combination, and this aided by the intervention of another affinity, not only not stronger, but actually weaker, might occasion the decomposition.

This cause is not less efficient in complex affinities, or it determines the union of the substances most disposed to assume the elastic form, and their separation as a volatile compound. "If, therefore, it be "desired to know the result of the exposure of two "salts, to the action of heat, it is only necessary to "consider which of the two bases, and which of the "two acids, have the greater volatility, if there be a "difference; for the more volatile base and acid will "escape, and enter into combination, and the fixed "base, and fixed acid, will remain behind, and com-"bine with one another *."

Researches, p. 3.

Such is the view given by Berthollet, of what are named Single and Double Elective Attractions. It is sufficient to have stated it fully in this part of the work, and to observe, that though there is every reason to admit much of it as just, some doubt may perhaps still remain, whether, in its whole extent, it is altogether just. Some observations on this subject will be found in a Note (A f).

Another subject belonging to the present section, and which has much occupied the attention of chemists, is that of determining numerically the forces of affinities among bodies. The usual measure of these forces, is that deduced from decomposition; we discover from it, that one body A, appears to have a stronger attraction to another B, than a third C has, because when B C are combined, A decomposes the compound, by attracting B. But admitting the justness of the inference, this affords us only very general information; it does not enable us to determine the real comparative forces; we learn nothing more, than that the attraction of one body is stronger than that of a third. The desideratum is to know, with precision, how much stronger it is; and were this done, it has been supposed that it would be of much utility in the science, as enabling us to discover, by calculation, what we can at present ascertain only by experiment. Different methods have been followed, in the attempts to solve this interesting problem.

Guyton had long ago observed, that when different metals were brought into contact with quicksilver,

they adhered to it with different degrees of force; and on multiplying his experiments, he found that the order of the forces of adhesion corresponded with the known affinities of the metals to quicksilver. The experiment was made with accuracy in the following manner: Plates of the different metals, of the same size and form, were prepared, and were suspended in the centre, from the extremity of the beam of a sensible balance. They were successively brought into contact with mercury, and made to slide along its surface; the mercury being changed at each experiment. The force with which they adhered was easily discovered, by the weights which it was necessary to attach to the other extremity of the beam, to raise each plate. The results are given by Guyton in the following table:

Gold adhered to mercury with a force of	446 grains.
Silver,	429
Tin,	418
Lead,	397
Bismuth,	372
Zinc,	264
Copper,	142
Antimony,	126
Iron,	115
Cobalt,	8

Guyton justly observes, that if we examine whence these differences arise, we find they cannot be owing to the pressure of the atmosphere; for it is the same with regard to all of them; nor to the different de-

grees of polish; for a plate of iron, unpolished, adhered more strongly, by several grains, than one of the same metal which had received a fine polishing; nor to the densities of the metals; for if this had been the cause, silver would have been beneath lead, and tin beneath iron. But the order of adhesion is precisely that of the order of affinities; gold is the metal to which quicksilver seems to have the strongest attraction; while, with iron or cobalt, it can scarcely be combined. Since these differences, therefore, arise from the different forces of attraction, subsisting between these metals and quicksilver, they may be regarded as numerical expressions of these forces, and may consequently be so far admitted in determining the general problem.

Unfortunately, however, experiments of this kind are too limited to be of much utility in this point of view; and when extended to other chemical agents, so many difficulties occur from mutual chemical action, and other causes, that the results cannot be regarded as sufficiently accurate to admit of any strict conclusion. In the further experiments of Achard on the same subject *, we accordingly find a number of facts, either incompatible with the general hypothesis, or not explained by it. The principle also is doubtful, as the results denote rather the facility of combination than the absolute force of attraction.

Wenzel had supposed, that the time requisite for a

* *Encyclopédie Methodique*, tom. i. p. 468.

combination being effected, is the measure of the force of the affinity exerted. The method he proposed to apply this principle, was to cover equal cylinders of different metals with a crust of varnish, leaving only one extremity uncovered. They were immersed in a common solvent, (nitric acid was what he employed), and according to his statement, on being removed at the end of a certain time, the quantities dissolved corresponded with the known affinities of the metals to the acid; and the affinity of the acid to each of the metals being inversely as the times necessary for the solution of equal quantities of them, the numerical expressions of these affinities might thus be easily obtained.

Independent of various objections, to which the experiment is liable, the principle on which the method is founded is altogether false. The facility or rapidity of combination, depends not on the abstract force of affinity, but on that modified by the cohesion, elasticity, and other qualities of bodies; and we meet with innumerable examples, in which a combination takes place slowly, where the attraction, from which it arises, appears to be strong, or where it is effected with facility, where the attraction is comparatively weak.

The resistance which is opposed by a combination, to the separation of its constituent parts, has been proposed as the measure of the strength of their reciprocal affinity. But we have no means of appreciating the resistance with accuracy. The intervention of a superior affinity cannot be employed; for the

strength of this affinity would first require to be ascertained. The only method that can be proposed, is by the degree of heat which may be necessary to effect the decomposition. But many compounds cannot be decomposed by heat; and in those which can, the decomposition is influenced as much by the comparative elasticity of the principles of the compound, as by the strength of affinity existing between them.

The method proposed by Mr Kirwan, is undoubtedly far superior to any other; and although, from the difficulties attending the necessary experiments, he may have failed in solving the problem, he has probably approached to the principle on which the solution is to be attempted,—that the power of producing saturation of properties by a body entering into a combination, is the measure of the force of its affinity. As a satisfactory statement of this, however, must involve considerable details, and as it can scarcely be considered as elementary, I have placed the whole discussion in a Note (A g).

The decomposition of a body, or its resolution into its constituent parts, forms what in chemical language is termed ANALYSIS; at least when such a decomposition is effected with the view of discovering its composition. Analysis, therefore, may be of two kinds, either as it is effected by the application of heat, or by the intervention of a superior affinity.

Thus it frequently happens, that when a compound is exposed to a high temperature, the force of attraction existing between its principles is weakened, and

they separate; and one of them, being in general more volatile than the other, is expelled. In other cases, a compound is not decomposed by the most intense heat: but if it be mixed with some other chemical agent, and placed under circumstances favourable to the exertion of chemical attraction, the substance mixed with it may combine with one of its component parts, when of course the compound will be decomposed, and from the products, its constituent principles may be ascertained.

These are examples of what is termed Simple or True Analysis. Complicated or false analysis is that where the composition of the compound is subverted, and its individual existence destroyed, but where, from the combinations of its principles in new modes and proportions, it is impossible to reproduce it by the combination of the products of the analysis.

Synthesis is the reverse of analysis. It is merely the reproduction of the substance, by the combination of the principles which the analysis discovered to be its constituent parts; and, when it can be effected, is regarded as the surest proof of the accuracy of the analysis. When these are combined in the investigation of the chemical constitution of any body, they give all the evidence which the science of chemistry can afford.

BOOK II.

OF IMPONDERABLE SUBSTANCES.

HAVING stated the general doctrines relating to the attractive powers which operate on the particles of matter, we have next to enter on the consideration of the repulsion by which these attractions are counteracted, and by which the particles of bodies are separated from each other.

Instead of considering repulsion as a general agency or force, philosophers, finding that the cause producing it is capable of being communicated from one body to another, and that some of the phenomena of its transition indicate it to be a distinct principle, have been disposed to regard it as a peculiar subtle kind of matter, the same with that to which the phenomena of heat have been referred, and which, in the modern chemical nomenclature, has been denominated Caloric.

Though the materiality of this power has not been strictly demonstrated, the supposition has much probability, and accords with nearly all the phenomena. Nor, considering it as an hypothesis, are we led into any error in treating of it as the cause of repulsion, since, whatever may be the nature of this power, whether it be regarded as a quality of bodies, a general force, or a distinct kind of matter, the same force or principle which produces the phenomena of heat, is undoubtedly that which counteracts the attractions exerted between the particles of bodies.

The connection of Light with Heat has long been observed, and has even led to the opinion of their identity. Whatever may be the nature of the chemical relation subsisting between them, it is at least so intimate, as to require them to be arranged under the same class; and light may, with still more propriety, be placed under this arrangement, as its particles are mutually repellent.

From heat and light there is a natural transition to the agent which gives rise to the phenomena of Electricity and Galvanism; and in this book I propose, therefore, to consider these principles as chemical powers.

The common character they possess, is that of not being subject to the attraction of gravitation, or at least their gravity is incapable of being appreciated. Hence they may be distinguished as a class, by the name of Imponderable Substances. They possess the

greatest subtilty or tenuity; we cannot easily insulate or obtain them in a separate state of existence; we observe them only in states of combination, or in their rapid transition from one body to another; we can scarcely discover their specific affinities or measure their force, and we are unable to trace their particular combinations, or consider them as essential constituent principles of any compound. They are also diffused over every kind of matter; at least caloric exists in all bodies, and probably also the electric and galvanic agents.

CHAP. I.

OF CALORIC.

THE terms Heat and Cold, employed to denote certain sensations, though incapable of strict definition, are sufficiently well understood. These sensations are excited by bodies applied to the organs of animals. It is observed, however, that the same body will, at different times, excite very different degrees of sensation, or even sensations totally dissimilar; being capable, at one time, of occasioning the feeling of intense cold; in a short time, it may convey an agreeable warmth; and by another change of circumstances, it will induce extreme heat. It is evident, therefore, that the power of inducing these sensations, does not depend upon the matter itself, which is applied to our organs; for every shade of sensation is produced, without the qualities of that matter being permanently changed. Hence the power of producing such sensations, is considered as depending not merely on the body itself, which is applied to our organs, but on a certain subtle principle, which is present in it, and which, according to its quantity, gives rise to different sensations. If the body applied contain a certain quantity of it, the sensation of heat is

excited; if the quantity be diminished to a certain extent, that of cold is produced, and the intensity of either sensation is proportioned to the accumulation or diminution of this principle.

Even in familiar language, this distinction is observed. If a piece of iron be made red-hot, we conceive that a quantity of what we call heat, that is, of a certain subtle power, has been introduced into it; and that the property the iron in this state has, of affecting the organs of animals in a peculiar manner, depends on the presence of this principle. When the iron is left to cool, we suppose merely, that it parts with its excess of heat; and accordingly, we find, that after a short time, it will excite the sensation only of gentle warmth. It may be cooled still farther, so as to induce, when applied to the surface of the body, the sensation of cold; and though this was once conceived to be owing to the introduction of a positive power, opposed in its nature to that of heat, the discoveries of philosophy have, even in this point, been transferred to common opinion, and the power the iron has in this example, of producing the sensation of cold, is considered as depending merely on its being still farther deprived of the principle of heat.

Such is the manner in which we are to view these phenomena. There exists a subtle principle or power, capable of being communicated to all bodies. When present in any body to a certain extent, it occasions, in animals, a certain sensation, that of heat; and the intensity of the sensation it excites, is proportioned to the quantity in which it is accumulated in that body.

When thus present in one body, it may be transferred from it to another, and then the power of exciting the peculiar sensation is also transferred. In the example we have taken, the piece of iron red-hot, may be deprived of its heat, by plunging it into water, and in this case the water becomes hot in its turn; the water may equally be deprived of it, and thus the excess of power may be transferred from one body to another, in whole or in part, until a perfect equilibrium is established.

Philosophers have further observed, other effects to result from the introduction of this power. When a body acquires the power of exciting a stronger sensation of heat, it is also invariably expanded; its volume is augmented in every direction. The piece of iron, for example, when hot, would occupy more volume than when cold. When, therefore, any hot body is cooled, the volume is diminished, and the diminution or increase of expansion, is proportioned to the abstraction or addition of the peculiar power on which these effects depend.

It has, lastly, been proved, that when the expansion arising from the introduction of this power, is carried to a certain extent, bodies change their forms, solids becoming fluids, and fluids being converted into vapours, or airs.

These effects being thus inseparably connected, have been considered as originating from the same power or principle; a principle, the existence of which is unquestionable, though its nature may be unknown.

This principle has been distinguished by various appellations, as Fire, Heat, the Matter of Heat, or the Igneous Fluid; terms which are either ambiguous, or which involve some hypothesis, and which are superseded by the unexceptionable appellation of Caloric.

By Caloric, then, is to be understood a power present in bodies, the cause of their expansion, and of their existence in the fluid and aëriform states; and which, when present in a certain quantity, excites in animals the sensation of heat; the sensation of cold being also the effect of its abstraction.

Respecting the nature of this power, different opinions have been entertained by philosophers; some consider it as a peculiar subtle fluid, diffused over matter, and capable of entering in greater or less quantity into every body: others have supposed all the phenomena exhibited by heated bodies, to arise merely from a peculiar state of these bodies, or, to speak more precisely, from a vibratory motion, more or less violent, of their minute particles.

It would be improper, on our very entrance on the consideration of Caloric, to engage in the discussion of this question, since it can only be determined from a full knowledge of the properties of this power, and its relations to other matter. Nor is it necessary at present to enter on any investigation of this kind, since whatever may be the nature of the power which the term Caloric expresses, its existence is sufficiently demonstrated, as the cause of certain effects; and although the nature of that cause may be unknown, the

effects themselves, their relations to each other, and the general laws according to which they are produced may be investigated with sufficient precision.

I shall deliver the chemical history of Caloric under the following sections. In the first, I may facilitate the prosecution of the subject, by taking a general view of the distribution of this power; in the second, I shall consider its effects on matter; in the third, the laws of its communication and propagation; in the fourth, the comparative quantities of it which bodies contain; in the fifth, the comparative quantities which the same body, in its different forms, contains; under the sixth, may be reviewed the opinions which have been advanced with regard to the nature of this power; and its chemical history may be concluded, with an enumeration of the causes by which its equilibrium is subverted, or heat and cold produced; and the applications of these to practical chemistry.

Sect. I. *Of the Distribution of Caloric, and the Measure of Temperature.*

The state of a body with respect to its power of producing the different effects arising from the presence of caloric, is termed its *Temperature*. In each body the temperature depends on the quantity of caloric which it contains. If at any temperature it contain a certain quantity, the addition of caloric raises

its temperature; in other words, the body now possesses the power of exciting either a weaker sensation of cold, or a stronger sensation of heat, and of producing in other bodies a greater degree of expansion.

Of these effects, that of exciting the sensation is so limited, and is so much influenced by the state of the sentient organ, as well as by other external circumstances, that it cannot be applied as a measure of temperature.

Expansion is an effect of caloric more regular and extensive, and is therefore now always employed to measure temperature. When two bodies produce the same increase or diminution of volume in a third body, to which they are equally applied, they are said to be at the same temperature; and any one body is said to be at a higher or lower temperature, according as it produces a greater or less expansion in another body with which it is in contact.

An instrument has been contrived, by which every degree of expansion can be accurately measured, and which is of course of the first importance in all our experiments on the subject of caloric. This instrument, termed the Thermometer, is of modern invention, the honour of which is due to Sanctorius, an Italian physician, who lived in the 17th century. He had observed the expansion which air suffers when it is heated, and it occurred to him that this expansion might be used as a measure of the variations of heat. His thermometer was simply a hollow glass ball, from which a long cylindrical tube, open at the extremity, issued. A small quantity of the air of

this tube is expelled, by applying heat to the ball. The open end is then immersed in a coloured liquor, either oil or spirit, and as it cools, a quantity of the fluid rises in the tube. A scale of equal parts is applied to the tube, and the extent of the expansion of air in the bulb, by heat, is accurately discovered by the descent of the coloured liquor, its condensation by cold being marked by its ascent. This instrument has the advantage of indicating very minute changes of temperature, air being so greatly altered in its volume by alterations of temperature, and on this account it may still be occasionally used with advantage for some purposes. It is otherwise a rude instrument, inconvenient, from its unwieldy form, liable to variations, from changes in the pressure of the atmosphere, and inapplicable to the measurement of any extensive range of temperature *.

An important improvement was made in the thermometer, by the members of the Academy del Cimento, by substituting a fluid as the measure of expansion, and inclosing it in a tube hermetically sealed, by which any effect arising from variations in the atmospheric pressure is avoided, and the instrument is rendered both more accurate and more manageable. Spirit of wine coloured was the fluid that was first

* Mr Leslie, as I shall soon have to remark, has, by his contrivance of the *differential thermometer*, which is an air thermometer, obviated some of these objections, and rendered it applicable, with peculiar advantage, to certain investigations.

employed. Mercury was afterwards used by Dr Halley and Sir Isaac Newton. Both fluids are still in use, each being adapted to particular purposes.

The thermometer constructed with either fluid, is merely a glass ball, with a long tube issuing from it, of a very small bore, and perfectly cylindrical, the bulb being entirely, and the stem partly filled with mercury or coloured spirit.

The principle on which the thermometer indicates temperature, is, that caloric has a tendency always to preserve an equilibrium; so that if two bodies, at different temperatures, be brought into contact, caloric will always pass from the one at the higher into that at the lower temperature, until the temperature of both is the same. When the thermometer, therefore, is applied to a hot body, it receives caloric; when to a cold one, it communicates part of its own caloric; and this communication continues until the thermometer and the body arrive at an equality of temperature. Now, the temperature of the thermometer is discovered from the volume the thermometrical fluid occupies in the instrument. At a certain temperature, it stands at a certain point. When caloric is communicated to it; in other words, when its temperature is raised, the fluid is expanded, and of course rises in the tube: when caloric is abstracted, it is contracted and descends; the changes of volume being accurately measured by a graduated scale attached to the tube. The point at which the fluid is stationary indicates its temperature; and, from the property of caloric, just stated, this again indicates the

temperature of the matter with which the thermometer is in contact. The instrument is made with a small ball, and with a tube of a very fine bore, that it may indicate changes of temperature more speedily and with more accuracy.

It is sufficiently obvious, that, strictly speaking, the observed changes of volume in the thermometrical fluid are not the real changes; for the glass ball is likewise expanded by heat, and contracted by cold, and, in the one case, must render the expansions apparently less than they really are, and in the other must equally diminish the contractions. Hence it is only the excess of the expansion or contraction of the fluid above that of the glass, that is observed. From the principle, however, on which the scale of the instrument is constructed, this does not introduce any error.

For some time after the invention of the thermometer, a great inconvenience was experienced in there being no fixed points of comparison, so that the observations made by one instrument might be compared with those made by another. The scale of each was entirely arbitrary, and the method by which it was first attempted to establish a correspondence between them, was to use tubes of the same length, and the same fineness of bore, and divide them into an equal number of degrees; a method obviously impracticable.

Various attempts were made by Boyle, Halley and others, to remedy this inconvenience, and at length two invariable points were established, which served as the basis of the thermometrical scale. For this we are indebted to Newton. It had been observed by Hooke, that water freezes or ice melts always at one

uniform temperature. If we immerse the thermometer in melting snow or ice, the fluid within will gradually sink to a certain part of the tube, where it will stop, and, however long we allow it to remain, it will descend no lower. And the experiment, if repeated at any time, or in any country, will afford the same result, the fluid always standing at the same part. If, therefore, we mark this, we obtain one fixed point, which must be the same in every thermometer. It had been observed by Hooke, likewise, that under the medium pressure of the atmosphere, water boils at one uniform temperature. If, therefore, under such a pressure, the thermometer be immersed in boiling water, the height to which the mercury rises in the tube will be always uniform, and this being marked, will afford another invariable point. These two, then, the point at which water freezes, and that at which it boils, may be connected by a scale divided into any number of equal degrees; and thus, whatever may be the length of the tube, or its diameter, the degrees marked upon it will correspond with those marked on any other on the same scale. This is accordingly the method according to which thermometers are always constructed. The scale adapted to them has been different in different countries, but when two points are thus fixed, which in all of them correspond to certain numbers, whatever names may be given to these numbers, or whatever may be the number of parts into which the scale intermediate between these points is divided, it is easy, by calculation, to bring them to correspond with each other.

In every thermometer, besides the scale between these two points, there is one divided into similar degrees, which descends from the freezing point of water, and another which ascends from that of boiling water *.

The thermometer commonly used in this country, is one first made by Fahrenheit, a German artist, and thence named Fahrenheit's. The lowest temperature marked upon its scale, is that produced by a mixture of snow and sea-salt acting on each other, this being the lowest temperature known in Fahrenheit's time †.

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* In the Principles of Chemistry, by Nicholson, is an excellent account of the details with regard to the construction and graduation of thermometers. Some circumstances not always attended to, but of importance in graduating them, are also pointed out in the report of a committee of the Royal Society, in the 67th volume of the Transactions of the Society. They state, in particular, the errors arising from plunging more or less of the stem in boiling water, in fixing the boiling point, (a circumstance, I may observe, for which in common thermometers a correction is requisite, in observing the higher temperatures), and from the variable pressure of the atmosphere, as affecting the boiling of the water, and recommend that the thermometer be adjusted either when the barometer is at 29.5, by immersing the ball in water, or at 29.8, by exposing it to steam.

† It is uncertain, however, in what manner Fahrenheit obtained this temperature from such a mixture, as, from mixing snow and salt, the temperature is 4°, or even

The range of temperature between it and the freezing point of water, he divided into 32 parts or degrees. That point, therefore, stands at the 32d degree. The part of the scale between the freezing and boiling points of water, is divided into 180 degrees. The boiling point, therefore, is 212°.

In France, the thermometer termed Reaumur's, was for a time very generally employed. In it the scale commences at the freezing point of water, which is therefore marked 0, or what is named the Zero. Between it and the boiling point of water, there is a scale divided into 80 degrees, the point at which water boils, being termed the 80th degree. To express higher temperatures, the scale is carried on, divided into degrees exactly equal to these; and in like manner, to denote diminution of temperature below the freezing point, a descending scale, divided into similar degrees, commences at that point. The correspondence between these two thermometers is easily found, by the following general formula: Each degree of Fahrenheit's scale is equal to $\frac{4}{9}$ths of a degree of Reaumur's. If, therefore, the number of degrees of Fahrenheit's, either above or below the freezing point of water, be multiplied by 4, and divided by 9, the quotient will be the corresponding number on Reaumur's. Or, to reduce those of Reaumur's to Fahrenheit's, they must be multiplied by 9 and divided by 4.

6° below the beginning of his scale.—*Philosophical Transactions*, vol. lxxviii. p. 304.

Besides these, other divisions of the thermometrical scale have been invented, but have fallen into disuse *. That of De Lisle's, in which the scale commences at the boiling point of water, and proceeds to the freezing point, through 150 degrees, is sometimes mentioned by authors; and the division of Celsius, which was used in Sweden, has been revived in France. It commences at the freezing point of water, and between that and the boiling point, is divided into 100 parts; hence it has been named the Centigrade Thermometer. This division is superior to that of Reaumur's, and is more simple than Fahrenheit's. Each degree of Fahrenheit's scale is equal to $\frac{5}{9}$ths of a degree of the centigrade scale. To reduce, therefore, the degrees of the former to those of the latter, the number of degrees of Fahrenheit above or below the freezing point of water are to be multiplied by 5, and divided by 9. Or, to reduce those of the centigrade scale to Fahrenheit's, their number must be multiplied by 9, and divided by 5.

Of these scales, the centigrade is perhaps the most natural division, and hence several British philosophers are disposed to receive it in place of Fahrenheit's. Fahrenheit's, however, has an important advantage, that the divisions are smaller, and hence it is much less requisite to use fractional parts, which, in simple observations, are apt to be neglected, and in calculation are inconvenient. It has another advantage, that the commencement of the scale being placed at a low tem-

* See Martine on Heat and Thermometers.

perature, we are seldom troubled with negative degrees; while, in the centigrade, and in Reaumur's scale, it is always necessary, either by prefixing the signs of plus and minus, or by terms, to denote whether the number stated is above or below the zero. Yet Fahrenheit's is after all a very arbitrary and inartificial division. It appears to me, that a scale might be formed, preferable to any we yet have, by taking, as the extreme points, the temperatures of freezing and boiling quicksilver; the one being —39° of Fahrenheit, and the other +672° *, and dividing the intermediate space into 1000 parts. The degrees would thus be smaller even than Fahrenheit's, without being too much so, to be inconvenient either in the construction of the instrument, or for observation; fractional parts might in general be entirely disregarded; and the commencement of the numeration being so low, we should scarcely ever have to express negative degrees. The commencement of the scale would also be about the lowest natural temperature. It seems the most natural method, too, to assume the freezing and boiling points of the fluid, which is the most accurate thermometrical one, and is most generally employed for that purpose, as the fixed points of the scale which its expansions are to measure. These points, by careful experiment, might be fixed with accuracy; and, in the construction of the instrument, the common method might still be followed, though the scale might be divided and numbered in relation to these points.

The fluid in these thermometers, I have already

* Ascertained by Irvine, with accuracy.

observed, is either mercury or coloured alkohol, and to certain purposes one of these is better adapted than the other. For common use, the mercurial is preferable to the spirit thermometer, because the expansions of mercury, from given alterations of temperature, are much more uniform than those of alkohol. It is therefore more accurate. It also suffers changes of temperature with more celerity, and is therefore more sensible; and to suffer any given alteration of temperature, it requires less caloric than any other. It can also measure higher temperatures. Alkohol is converted into vapour at 182° of Fahrenheit; it can therefore be used only to measure temperatures inferior to this, while mercury is not converted into vapour under at leaſt 650°. Alkohol, however, has the opposite advantage, that of being capable of measuring very low temperatures, mercury becoming solid at 39° below o of Fahrenheit, while alkohol has not yet been frozen, and can therefore be employed to measure the most intense colds. Its changes of volume are also more regular at these low than they are at high temperatures. And, at all temperatures at which it is practicable to apply it, its expansions from given changes of temperature are greater than those of other fluids; hence the changes in the thermometrical scale, constructed with it, are more conspicuous; but, at the same time, as its expansibility very sensibly augments with its temperature, they are less accurate, and the ratio of expansibility varying, too, with its concentration, another source of error is introduced. The degree of expansion can be rendered apparent to

as great an extent in quicksilver, by using a tube of a very fine bore, while in alkohol this cannot be done to the same extent, from the error introduced by its adhesion to the tube. Hence, perhaps, for every purpose except that of measuring very low temperatures, the mercurial thermometer should be preferred to that with alkohol. Oil has scarcely any advantage as a thermometrical fluid, and its viscidity causes it always to adhere more or less to the tube.

In order that the thermometer might be employed, with certainty, as an instrument for measuring variations of temperature, it was necessary to ascertain, whether the expansion and contraction of the thermometrical fluid corresponded, in every degree, to the addition or abstraction of caloric. If the addition of a certain quantity of caloric, at a low temperature, cause less or more expansion than the addition of an equal quantity, at a high temperature, it is evident, that the information we receive from the instrument is not accurate.

Experiments have therefore been made, to determine this point. The subject had engaged the attention of Halley, Dr Brooke Taylor, Dr Black and others, and the same general experiment was made to determine it. It consisted in selecting a thermometer, the tube of which was perfectly cylindrical, immersing it in hot water, and marking the point at which the thermometrical fluid stands; then immersing it in an equal weight of cold water, and again marking the part of the scale where it is stationary; lastly, mixing the two portions of water, and observing at what

point the fluid of the thermometer immersed in the mixture stands. If the temperature indicated be the exact mean between the two temperatures, it may be concluded, that the expansions proceed equally, and, of course, that the indications will be correct; while, if it differ from the mean, it must be concluded, that the ratio of expansion is unequal. The experiment requires much care, in the execution to guard against sources of error, particularly from the effect of the vessel on the temperature of the mixed fluid, and the abstraction of heat by the air, or by the escape of vapour. It was executed with much attention by De Luc, at an early period, and the result was, that the different thermometrical fluids did not expand in an uniform proportion to the quantities of caloric they received, but proceeded in an increasing ratio, as the temperature was varied.

Quicksilver was by far the most regular; yet, even in it, the deviation was very apparent. When a quantity of water at 45° was mixed with an equal weight at 200.7° the mercurial thermometer, put into the mixed fluid, indicated the temperature to be 2.5 degrees less than the arithmetical mean; and when the experiment was made at other temperatures, corresponding results were obtained *.

With other fluids the deviations were still greater. While the mercurial thermometer, placed in water of the precise mean temperature between 32° and 212°,

* *Recherches sur les Modific. de l'Atmosph.* t. i. p. 298. 302.

instead of indicating that mean 122° stood at 119°; a thermometer with olive or linseed oil was still farther from the mean, or indicated only 117°, one with alkohol 108°; and so great was the irregularity in water, that its indication was only 75° *. Hence the great superiority, in accuracy, of the mercurial thermometer.

It follows, however, from the deviation from equality in the expansions even of quicksilver, that the thermometer constructed with it, though the most accurate of any, cannot, according to the common division of the scale, be considered as an exact measure of temperature. When it indicates a temperature, for example, as 119° the real temperature, according to De Luc's estimate, is 122°. This might be obviated, by accommodating the degrees on the scale to the real expansions †; and when delicate investigations on temperature are required, a thermometer on this construction ought always to be employed. In the common construction of the instrument this is not attended to; and hence the advantage of a table which shall point out the correspondence between the apparent and the real indications. De Luc has given one from the above experiments, adapted to Reaumur's scale, to which I have added the corresponding numbers on the scale of Fahrenheit, as it is generally used in this country. The two extreme points, those of the freezing and boiling of water, are supposed to be accurately determined in

* *Recherches*, t. i. p. 311.

† Ibid, t. i. p. 307.

the thermometer; and as these are receded from, the deviations from the real temperature, in the temperatures which the mercurial thermometer indicates become greater. The first column, according to each scale, expresses the real temperatures, and the second the corresponding temperatures on the mercurial thermometer, graduated in the common manner.

Reaum.	Reaum.	Fahr.	Fahr.
80	80.	212.	212.
75	75.28	200.75	201.38
70	70.56	189.5	190.76
65	65.77	178.25	179.98
60	60.96	167.0	169.16
55	56.15	155.75	158.34
50	51.26	144.5	147.33
45	46.37	133.25	136.33
40	41.40	122.	125.15
35	36.40	110.75	113.86
30	31.32	99.5	102.47
25	26.22	88.25	90.99
20	21.12	77.	79.52
15	15.94	65.75	67.86
10	10.74	54.5	56.16
5	5.43	43.25	44.22
0	0	32.	32. *

Dr Crawford, to whom, in his researches on heat, the determination of this point was of primary im-

* *Recherches*, t. i. p. 309.

portance, repeated these experiments. He likewise found, that the mercurial thermometer always indicated less than the mean temperature, though the deviation was not so great as in the experiments of De Luc, being, on an average, little more than 0.5 of a degree, when the difference of temperature between the two portions of water amounted to 100 degrees *; and, according to a correction he afterwards made, not more than 0.25° †.

This result was confirmed by an experiment, made in a manner somewhat different. A mercurial thermometer was suspended in an apparatus, in which it was equally exposed to the influence of air, cooled by snow to 32°, and of air heated by watery vapour to 212°. It rose to 121°, and remained stationary at that for fifteen minutes, the time during which the experiment was continued. It indicated, therefore, a temperature one degree inferior to the arithmetical mean, when the difference of temperature amounted to 180 degrees ‡, which agrees nearly with the result of the preceding experiment. Even this deviation from the precise arithmetical mean is diminished, by admitting a correction for the effect of the temperature on the quantity of fluid in the stem of the thermometer §.

In these experiments, the deviation of the mercurial thermometer from perfect accuracy is considerably less

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* Experiments on Animal Heat, p. 19.

† Ibid, p. 488. ‡ Ibid, p. 40.

§ Ibid, p. 48.

than that stated by De Luc; and the latter philosopher admitted, even from some considerations, that it might be less than appeared in his experiments. Perhaps, on the other hand, it is stated at less than it really is, in Dr Crawford's experiments. If these, however, are correct, and there is much reason to confide in his accuracy, it will follow, that though the mercurial thermometer does not measure temperature with perfect accuracy, the deviation is so inconsiderable, as to give rise to a very trivial error, in indicating temperatures between the boiling and freezing points of water; and that the preceding table gives differences too great between the observed and real temperatures. Above 212, the irregularities in the expansions of mercury become greater; and, in other fluids, they are so considerable, as to render them unfit to measure temperature with accuracy. The inaccuracy, it is obvious, in all these cases, arises from the expansibility of fluids, augmenting as their temperature is raised.

The thermometer, on the construction hitherto described, is necessarily very limited in its application. When made with alkohol, it can be used, indeed, to measure the most intense colds. But it cannot, even when mercury, the least volatile liquid, is used, be applied to indicate very high temperatures, as, at such temperatures, the fluid must be converted into vapour, and burst the tube.

To supply this deficiency, and to measure high temperatures, various methods have been proposed. A very ingenious one was employed by Newton. Assuming that the quantities of heat lost by a body in

small portions of time, are proportional to the excess of its temperature above that of the surrounding medium; or that, taking the times of cooling in arithmetical progression, the decrements of heat will be in a geometrical one; and observing the time of cooling, until the temperature is sufficiently reduced to admit of being accurately measured in some other mode, the original temperature may be discovered, and the highest temperatures thus measured. By this method, Newton determined various high temperatures, such as that of ignition, visible in the dark which he stated at 635° of Fahrenheit, and in day-light at 1000°; and it was afterwards applied by Dr Irvine, as well as by Dr Crawford, in their delicate experiments on the absolute heats of bodies, this being the only mode in which they could determine, with any accuracy, the quantities of heat lost by bodies mixed together at different temperatures, during the short time which elapses before a common temperature is formed *.

Different instruments, (named Pyrometers, as being thus applied to measure great heats), have also been invented for this purpose; of the greater number of which, it is scarcely necessary to give a detailed account. The difficulty of contriving an unexceptionable instrument of this kind, has arisen partly from the difficulty of finding a substance not liable to be altered by a high temperature, and which shall suffer a

* Crawford on Animal Heat, p. 99.

change of volume, sufficiently perceptible to be accurately measured; and partly from that of finding a measure, which shall not itself be affected by the high temperature, and be, at the same time, sufficiently delicate.

The pyrometer in which, perhaps, these difficulties have been most effectually surmounted, and which has come into most general use, is that invented by the late Mr Wedgwood. The pure earth named Argil, and the different earths (the clays) in which it predominates, have the singular property of not expanding, but of contracting by heat. This contraction begins to become evident, when the clay is raised to a red heat, it continues to proceed until it vitrifies, and the total contraction, in pure clays, exceeds considerably one-fourth part of the volume in every direction.

It occurred to Mr Wedgwood, that from this property, it might be employed in the construction of a pyrometer. The contraction the clay suffers is permanent, or it does not return to its former dimensions when cold. The degree of contraction it has suffered, therefore, can be ascertained without any source of fallacy, and will indicate the extreme of temperature to which it has been exposed.

This pyrometer consists of a gage, composed of two straight pieces of brass, twenty-four inches long, divided into inches and tenths, and fixed in a brass plate, so as to converge; the space between them at the one extremity being five-tenths of an inch, and at the other three-tenths. The pyrometrical pieces of clay

are small cylinders, flattened on one side, made in a mould, so as to be adapted exactly to the wider end. It is evident, that in exposing one of these pieces to a high temperature, the contraction it has suffered may be measured, by the length to which it can be slid into the converging groove or gage *.

The utility of this instrument, it was obvious, would be much increased by connecting it with the mercurial thermometer, and by ascertaining the proportion between the degrees of each; and this was done by Mr Wedgwood. The scale of his pyrometer commences at red-heat fully visible in daylight. The mercurial thermometer cannot easily measure any temperature above 500° or 550°; and hence, between the termination of the scale in the one, and its commencement in the other, there is a range of temperature requiring to be measured. This Mr Wedgwood did, by the expansions of a square piece of silver, measured in a gage of earthen-ware, constructed in the same way as his pyrometer; and by the same method, he found out the proportion between each degree of his scale, and that of any of the usual thermometrical scales. Each degree of his pyrometer he found to be equal to 130° of Fahrenheit. The commencement of his scale, or the point marked 0, corresponds with 1077½° of Fahrenheit's scale. From these data, it is easy to reduce either to the

* Philosophical Transactions, vol. lxxii. p. 310.

other, through their whole range. The scale of Wedgwood includes an extent of temperature equal to about 32,000° of Fahrenheit, or 54 times as much as that between the freezing and boiling points of mercury *. Its commencement, as has been stated, is at 1077½° of Fahrenheit, or red heat fully visible in day-light; its extremity is 240°; but the highest heat that he measured with it is 160°, or 21,877° of Fahrenheit; being the temperature of a small air-furnace, and 30° of his scale above the point at which cast-iron melts.

With regard to the accuracy of this pyrometer, Mr Wedgwood found from experience, that the pyrometrical pieces were liable to suffer variable contractions from circumstances, in their preparation, apparently minute, several of which he has fully pointed out †. A source of error not so easily remedied is, that natural clays, taken even from the same bed or stratum, and apparently of similar qualities, differ considerably in the contractions they suffer; and the kind of clay which Mr Wedgwood first employed having been exhausted, he found it difficult to substitute any other, the contractions of which corresponded with the scale he had originally constructed. He was under the necessity, indeed, at length, of making an artificial compound, of a clay, with argillaceous earth precipi-

* Philosophical Transactions, vol. lxxiv. p. 368.

† Ibid. vol. lxxvi. p. 390.

tated from alum *; but it may be doubted, whether such a composition can always be obtained uniform, and there is also some reason to doubt if these latter pyrometrical pieces give precisely the same indications as those Mr Wedgwood first employed, and from which he constructed his scale.

More lately, Guyton has proposed a pyrometer for measuring high temperatures, in which platina, a metal not fusible even at very intense heats, is employed as the measure of expansion. A rod or plate of this metal is placed horizontally in a groove framed in a mass of hardened white clay; one extremity of the rod is supported on the mass which terminates the groove; the other presses against a bended lever of platina, the longest arm of which forms an index to a graduated arc. The expansion which the rod of metal suffers from exposure to heat, is indicated by the change of position in this index. The mass of clay being highly baked, will not introduce any important error from its contraction; and the expansion which it may suffer during the exposure to heat, will affect only the small distance between the axis of motion of the index, and the point of contact of the plate, so as rather to diminish the effect than to increase it. Platina having the important advantage of not melting by any heat we have to measure, and of not suffering any chemical change from it, is well adapted to the construction of a pyrometer †.

* Philosoph. Trans. vol. lxxvi. p. 401.

† Nicholson's Journal, vol. vi. p. 89.

Besides these, various metallic pyrometers have been invented capable of measuring low temperatures, by the expansion being multiplied by the aid of wheels, levers, or other mechanical contrivances, or being magnified by microscopes. Such are the pyrometers of Muschenbroeck; that described by Ferguson; one invented by Mr Ellicot, with which he measured the expansions of various metals *; one by Mr Smeaton, and applied to the same purpose †; Mr Ramsden's, superior to the preceding ones in delicacy and accuracy ‡; Mr Crichton's, in which advantage is taken of the difference of expansion between a rod of zinc and a rod of iron, to give a curvature to the bar composed of the united rods, proportioned to the temperature to which they are raised; by which bending, motion is given to an index that at its other extremity, where the scale is marked, describes a considerable space ||; and, lastly, one by Regnier, on a principle somewhat similar, of which a report is presented to the French National Institute §. The strict accuracy of these instruments may, from the nature of their construction, be regarded as doubtful.

Since the employment of the thermometer, or rather of the expansion of bodies, as a measure of their temperature, more just and enlarged views have been

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* Philosoph. Trans. vol. xlvii.

† Ibid. vol. xlviii. ‡ Ibid. vol. lxxv.

|| Philosoph. Magazine, vol. xv.

§ *Mémoires de l'Institut National*, tom. ii.

acquired, of the distribution of caloric. While the property of exciting the sensation of heat, was the only one by which that power was characterized, or, indeed, the only property which it was known to possess, it seemed an obvious and just conclusion, that those bodies which did not excite that sensation, contained none of it. It was then accordingly the philosophical, as it is still perhaps the popular opinion, that bodies exciting the sensation of heat, contain the power termed Heat or Caloric, while those which do not excite this sensation, or which excite the sensation of cold, are supposed to be totally deprived of it, or even to have imbibed a positively frigorific power, directly opposite in its nature to the other.

These notions are now, however, justly exploded. We know, that at the most intense colds, all bodies still contain an immense quantity of caloric, since large quantities of it can be abstracted from them by artificial means, and since even these means are very far from being able to abstract the caloric entirely. It may not be uninteresting to state the facts on which this view of the extent of the distribution of caloric is established.

That the sensation excited by a body, is no accurate test of the caloric it contains has already been mentioned, and may be rendered evident, by stating the manner in which these sensations are excited. The temperature of the human body is generally about 96° of Fahrenheit. When any substance at a higher temperature than this is applied to our organs, it gives caloric to the part to which it is applied, and

this excites the sensation of heat. When, on the contrary, any substance is applied at an inferior temperature, it abstracts caloric, and this gives rise to the sensation of cold. Our sensations, however, are all of them much influenced by preceding impressions. Our body is constantly surrounded with air, at a temperature always inferior, at least in this climate, to the animal temperature; it is therefore always abstracting caloric from us; hence it happens, that if a body is applied to our organs, inferior to their temperature, but superior to the temperature of the surrounding atmosphere, the abstraction of caloric which it makes is inconsiderable, and, compared with the impression which the air makes upon us, it seems positively warm. In general, then, it may be affirmed, that whatever communicates caloric to our body, produces the sensation of heat; and that whatever abstracts it, causes the sensation of cold; but that, that abstraction requires at least to be greater than that made by the surrounding atmosphere, in order to convey to us the sensation of positive cold. Two bodies, also at the same temperature, will occasion different sensations, according to the rapidity with which they absorb or give out caloric. A piece of iron, at 32°, will feel much colder than a piece of wood at that temperature, merely because the former abstracts from the hand, or whatever part of the body touches it, caloric much more rapidly than the other; and, for the same reason, if the iron be at a high temperature, it will feel hotter than the wood at the same temperature.

From these circumstances, it is evident, that the sensation excited by a body is no accurate measure of the caloric it contains; and that the sensation of cold will be excited by any substance whose temperature is inferior to the temperature of the animal body, though that substance may, and actually does, contain a very large quantity of caloric.

That bodies at such a temperature do contain caloric, is proved, in the first place, By the expansion which they produce in the thermometer, if its temperature has been previously reduced, and if it is then applied to them; an expansion which could arise only from the communication of caloric. Or the contractions of the thermometrical fluid itself, shew this in a very simple manner. If the thermometer is applied to water which is freezing, the mercury will stand at 32°; but even in the cold of this climate, it falls occasionally much lower. At 32°, therefore, the mercury must have contained caloric, since it is only by the abstraction of that power that it could contract, and of course descend in the scale. At Hudson's Bay, the mercury has been observed to have descended to 50° below 0 of Fahrenheit, or 82° below the freezing point of water. At all degrees above this, therefore, it must have contained caloric; and even at that intense cold of which it is difficult to form a just conception, it must have contained much caloric, since by artificial means, we can sink it still lower; and if the mercury in the thermometer contained caloric at these extreme colds, all other bodies must have contained it, since it is the property of this

power to diffuse itself until an equilibrium of temperature be formed; nor can it be accumulated in one body without being present in the contiguous matter.

Even at these very low temperatures, there is not the least reason to believe, that bodies were near to being deprived of their caloric, since, even then, their particles must have been far from being in actual contact; and it is only by the repulsive power of caloric that their particles are kept asunder. This affords a still more extensive view of the distribution of this power. A solid body is to be conceived of, as consisting of a number of particles of the same nature, kept at certain distances from each other, by the agency of caloric. When a portion of it is withdrawn, these particles approach nearer to each other; and hence the contraction of volume that takes place. But any condensation hitherto effected, is very far from that in which these particles would be in contact, nor perhaps is such a condensation possible.

It has farther been established, that the fluid and aëriform states of bodies, are owing to the presence of caloric, a fluid being merely a solid reduced to the fluid form by its operation; an air, a fluid brought to the elastic state by the same cause. As there are many fluids, which require to be exposed to the most intense cold, in order to render them solid, and some which have not even yet been frozen; and as of the airs, scarcely one has yet been brought to the fluid state by the most extreme artificial cold, the conclusion follows, that the lowest temperature yet

produced is far from that point at which caloric would be entirely abstracted. This point, according to a calculation afterwards to be stated, from principles not improbable, is at least 900° of Fahrenheit's scale from the freezing point of water. "We are there-"fore," says La Place, "to consider all bodies on "this earth, and this planet itself, as penetrated with "an immense quantity of caloric, of which it is im-"possible for us to deprive them entirely, to what-"ever degree we may diminish their temperature." It is a portion of this caloric that is so frequently disengaged and rendered sensible by chemical action, as in the familiar example of combustion.

SECT. II. *Of the Effects of Caloric.*

THE effects produced by the operation of Caloric on matter are Expansion, Fluidity, Vaporization, and Ignition. Of these, Expansion is the most general, and may first be considered.

EXPANSION.

When a body, at any temperature, is brought into contact with another, the temperature of which is higher, a quantity of caloric passes from the latter into the former. The body which receives the caloric is expanded, or has its volume enlarged in every direction. This expansion is sufficiently evident in the thermometer when exposed to heat. Both

the glass and the thermometrical fluid are expanded, but the expansion of the fluid being greater, it ascends in the tube. In every body receiving caloric, with the few exceptions to be afterwards mentioned, when its volume is accurately measured, it is found to be enlarged.

When caloric is withdrawn, contraction, or diminution of volume as invariably follows. The particles approximate, and the body returns through the different degrees of expansion it had suffered when caloric had been communicated to it, until it arrives at its original volume. This also is evident in the descent of the thermometrical fluid, when the thermometer is exposed to cold; and the descent continues in proportion as caloric is abstracted.

The first important fact to be observed with regard to expansion is, that it is extremely different, in different bodies, from the same change of temperature, being in general less as the density of the body is greater. In solids, it is so inconsiderable, as not to be perceived without very accurate measurement; in fluids, it is much more evident; and in airs or vapours, the least alteration of temperature is accompanied by a very perceptible change of volume.

If we descend to a more minute examination of the degrees of expansion, we find, that in each of these classes of bodies, it is still extremely various. In solids, as the expansion, from a moderate change of temperature, is inconsiderable, the difference is less obvious; but still, in those which have been the subject of experiment, it has been observed. A knowledge

of the expansibilities of the different metals is of much importance in different arts, and more particularly in the construction of time-pieces; and on these, therefore, experiments have been most frequently made. The first having any pretensions to accuracy, are those made by Mr Ellicot, when engaged in prosecuting his method of correcting the irregularities in the motions of time-pieces, from the influence of heat and cold, on the length of the pendulum. He gave the following table of the proportions in the expansions of different metals by the same degree of heat:

Gold,	Silver,	Brass,	Copper,	Iron,	Steel,	Lead,
73°	103°	95°	89°	60°	56°	149° *

A more extensive table was given by Mr Smeaton, as the result of experiments he made with a pyrometer of his invention. The table indicates how much a foot in length, of each substance, gains in length, by an increase of temperature corresponding to 180° of Fahrenheit's thermometer, or to the difference between freezing and boiling water, expressed in such parts of which the unit is equal to the 10,000th part of an inch.

White glass barometer tube,	100
Antimony,	130
Blistered steel,	138
Hard steel,	147
Iron,	151

* Philosophical Transactions, vol. xlvii. p. 485.

Bismuth,	167
Copper hammered,	204
Copper, 8 parts, with 1 of tin,	218
Cast brass,	225
Brass, 16 parts, with 1 of tin,	229
Brass-wire,	232
Speculum metal,	232
Brass, 2 parts, with 1 of zinc,	247
Fine pewter,	274
Grain tin,	298
Lead, 2 parts, with 1 of tin,	301
Zinc, 8 parts, with 1 of tin,	323
Lead,	344
Zinc,	353
Zinc hammered,	373 *

Lastly, General Roy ascertained, by a pyrometer invented by Mr Ramsden, the expansions of glass and various metals, in parts of an inch, by 180° of Fahrenheit, or a rise of temperature from 32° to 212°.

	Inch.
Brass on one foot, in one variety,	0.0001237
——— in another,	0.0001262
——— in a third,	0.0001263
Steel rod,	0.0000763
Cast iron,	0.0000740
Glass tube,	0.0000517
Solid glass rod,	0.0000539 †

* Philosophical Transactions, vol. xlviii. P. II. p. 612.

† Ibid. vol. lxxv. p. 473.

Mr Troughton has since stated the expansion of brass and steel somewhat different; that of brass from 60° of temperature being 0.000640 on an inch, while according to Smeaton it is 0.0006444, and according to Roy, 0.0006316; that of steel he found to be 0.0003966, Smeaton stating it at 0.0003833, and Roy at 0.0003816. Variations of this kind will probably always be found where simple metals are not employed.

We perceive from these tables very little connection between the expansibility of solids and any of their physical or chemical properties. That it has no relation to their density, either directly or inversely, is very well shewn in the table of Ellicot, where gold is at one extremity and lead at the other, though these two approach nearest in density, while copper, iron, &c. are placed between them; and this is also obvious from many examples in the other tables. There is some relation between the expansion and the fusibility; those which are most fusible, as antimony, bismuth, tin, lead, and zinc, expanding most; and indeed, in the entire table of Ellicot, the expansions are stated almost precisely in the order of the fusibilities. But this law also does not hold in a variably, as will be apparent from the table of Smeaton, where antimony, for example, is stated as expanding less than iron, and bismuth less than copper, though such deviations may in part arise from the errors to which all these experiments must still be considered liable.

The expansion of solids from heat is a source of error in the construction of time-pieces, the pendulum

being lengthened or shortened according to the temperature, and of course its motions varied. This error is corrected by opposing the expansion of one metal to that of another; so that in a compound pendulum, composed of two metals, properly adjusted according to their expansibility, the expansion of the one is counteracted by that of the other, and the length remains unaltered, or the centre of oscillation of the pendulum remains always at the same distance from the point of suspension. This ingenious mode of remedying the deficiency to which time-pieces are liable, appears to have occurred to the artists Graham and Harrison; the application of it was executed by them in different methods *, and since their time has been frequently varied.

In fluids, a similar difference of expansion from a given change of temperature is observed as in solids, and as their expansions are greater, these differences are even more conspicuous. Thus, the expansion of water from a given change of temperature is greater than that of quicksilver from the same change, and the expansion of alkohol is still greater than that of water. Taking as a standard of comparison the expansions they suffer in the rise of temperature from 50° to 100° of Fahrenheit; that of quicksilver is not more than $\frac{1}{50}$ of its volume at 50°; that of water about $\frac{1}{11\frac{1}{3}}$ of its volume at the same temperature; while that of alkohol is not less than $\frac{1}{3\frac{1}{3}}$. The differences in the expansibilities of different liquids is not

* Philosoph. Trans. vol. xlvii. p. 517.

precisely in the same proportion at every temperature, as will immediately appear; but the general difference remains, or in the examples here given, at all temperatures alkohol is more expanded than water, and water more than quicksilver.

Since the expansions, both of different solids and of different liquids, are thus unequal from equal changes of temperature, it might be expected that the same law would be observed in the expansions of aëriform fluids, or that different bodies existing in the aërial state would likewise expand unequally by the same change of temperature. That such was the law was at one time generally admitted, and numerous experiments were made to determine the relative expansions of the different aëriform fluids, both those which are permanently elastic, and those which exist as vapours. Besides the experiments which were made at an early period of the investigation, the subject occupied the attention of Roy, Saussure, Priestley, Monge, Guyton, and other philosophers, but the results of their labours were extremely discordant. Priestley, who was the first that attempted to ascertain the comparative expansions of different aërial fluids, assigned to them very different proportions, some expanding two or three times more than others *. At a later period similar experiments were executed by Guyton and Duvernois, and they also found, that the aërial fluids expanded very unequally from the same augmenta-

* Experiments and Observations on Air, vol. iii. p. 452.

tions of temperature. The following table shews the total dilatation the airs suffered in being heated, from 32° to 212° of Fahrenheit.

Atmospheric air,	$1\frac{1}{.067}$
Oxygen gas,	$4+\frac{1}{2.09}$
Nitrogen gas,	$5+\frac{1}{1.062}$
Hydrogen gas,	$\frac{1}{2.55}$
Nitrous gas,	$\frac{1}{1.65}$
Carbonic acid gas,	$1+\frac{1}{106.3}$
Ammoniacal Gas,	$5+\frac{1}{1.248}$

A very extensive table, founded on these experiments, is given by Prony, of the dilatations of the different elastic fluids at every temperature, measured by the centigrade thermometer, from the freezing to the boiling points of water, and also curves by which they are represented *.

This subject has since been investigated by Mr Dalton and by Gay Lussac, and their experiments agree in establishing the general result, that all the aëriform fluids suffer the same expansion from equal augmentations of temperature.

From Gay Lussac's experiments, which seem to have been made with much accuracy, and with an apparatus not liable to error, it appears, that 100 parts of atmospheric air are expanded by an elevation of

* *Journal Polytechnique*, cahier ii. 65.

temperature from 32° to 212° of Fahrenheit, to 137.5 parts, this being the mean result of six experiments, which differed little from each other. Hence, if the total augmentation of volume be divided by the number of degrees which produced it, or by 180°, it will be found, that the expansion for each degree of Fahrenheit's scale is $\frac{1}{480}$ of the original volume. The mean expansion of hydrogen gas by the same elevation of temperature was 137.52; of oxygen gas 137.48; and of nitrogen gas 137.49; differences so trifling, that they may without hesitation be ascribed to the impossibility of rendering the circumstances perfectly the same in all the experiments, and indeed they are not greater than what appeared in the different experiments on atmospheric air. The experiments were extended, by a variation in the apparatus, to gases which are soluble in water; and the expansions of carbonic acid gas, muriatic acid gas, sulphureous acid gas, nitric oxide gas, and ammoniacal gas, by comparison with those of atmospheric air, were found precisely the same. The conclusion follows, therefore, that all the gases undergo the same dilatation from the same elevation of temperature. Of the vapours, that of sulphuric ether being the most easily managed, was submitted to experiment by Gay Lussac; and, by comparing its expansions above the temperature of 167° with those of atmospheric air, he found them to be precisely alike *.

* *Annales de Chimie*, t. xliii. p. 87. Nicholson's Journal, Oct. vol. iii. p. 207.

Mr Dalton's experiments, which preceded by some months those of Gay Lussac, were made by a very simple apparatus, and they too establish the conclusion, that aëriform bodies, at least atmospheric air, hydrogen gas, oxygen gas, nitric oxide gas, and carbonic acid gas, which were those submitted to trial, undergo the same expansions from the same augmentations of temperature, 100 parts expanding in the rise of temperature from 55° to 212° to 132.5 *. This gives as the expansion from 32° to 212° 137.3. The result of Gay Lussac's experiments is, as has been already stated, 137.5. The expansion, therefore, for each degree, according to the former, is $\frac{1}{483}$, according to the latter $\frac{1}{480}$, an agreement as near as can be expected in experiments of this nature. The errors and discordant results in former experiments had arisen, as both Dalton and Gay Lussac have remarked, principally from small but variable quantities of water having been admitted into the apparatus, which, passing into vapour as the temperature was raised, added to the volume of the aëriform fluid.

Bodies, therefore, existing in the aëriform state, differ remarkably from liquids and solids, in their expansions being all alike from given changes of temperature.

Another important fact to be illustrated with regard to expansion, is its progression with regard to temperature. It is obvious, that the progression may be regular, the expansion increasing precisely as the temperature rises, so that a double elevation of temperature

* Manchester Memoirs, vol. v. p. 595.

shall produce a double expansion; or it may proceed either in an increasing or decreasing ratio.

With regard to liquids it has been established, that the expansion does not proceed in an equal ratio, according to the increase of temperature, but is different at different parts of the thermometrical scale. If to water at 50°, a certain quantity of caloric be added, so as to produce a certain degree of expansion, if an equal quantity of caloric be added to the water at 60°, it will produce a different degree of expansion, and the same difference will be observed in any other temperature, and with every other fluid, though in different degrees.

The expansion in fluids is always in an increasing ratio, or if a given quantity of caloric produce a certain degree of expansion in a fluid at a low temperature, it will occasion a greater expansion at a high temperature. Hence the expansiblity of any fluid is least near to its freezing, and greatest near to its boiling point, and the differences between these extremes is in some of them considerable. This is very evident in water, in which the difference is more conspicuous than in any other fluid, and at the two extremes is very great, owing in a great measure to a singularity afterwards to be pointed out, in its change of volume from 40° to 32°. In cooling, one-eight part of the interval between the boiling and the freezing points, or $22\frac{1}{2}$ degrees of Fahrenheit's scale, the condensation will be, as ascertained by Count Rumford, as follows:—

In cooling $22\frac{1}{2}$,	from 212°	or to $189\frac{1}{2}$	18 parts.
——	$189\frac{1}{2}$ ——	167	16.2
——	167 ——	$144\frac{1}{2}$	13.8
——	$144\frac{1}{2}$ ——	122	11.5
——	122 ——	$99\frac{1}{2}$	9·3
——	$99\frac{1}{2}$ ——	77	7·1
——	77 ——	$54\frac{1}{2}$	3·9
——	$54\frac{1}{2}$ ——	32	0.2 *

From this it appears, without taking into account the proportion at the bottom of the table, where the irregularity alluded to exists, that the expansion of water in being heated $22\frac{1}{2}$ degrees to its boiling point, is more than five times greater than the expansion it suffers in being heated the same number of degrees from about the medium natural temperature.

In alkohol we perceive a similar progression in its expansibility, as the temperature rises. De Luc has given the following table, which exhibits this by a comparison with the expansions of mercury, in the mercurial thermometer, according to Reaumur's scale, assuming these, for the sake of a standard, to be regular † :—

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* Essays, vol. ii. p. 284.

† *Recherches*, t. i. 252.

Mercurial Therm.	Alkohol Therm.	Augmenting expansions of Alkohol, in this range of temperature.
80	80.0	6.2
75	73.8	6.0
70	67.8	5.9
65	61.9	5.7
60	56.2	5.5
55	50.7	5.4
50	47.3	5.1
45	40.2	5.1
40	35.1	4.8
35	30.3	4.7
30	25.6	4.6
25	21.0	4.5
20	16.5	4.3
15	12.2	4.3
10	7.9	4.0
5	3.9	3.9

The deviations from regularity in the expansions of quicksilver, are much less than in any other fluid, as has already been observed in pointing out its fitness for the construction of the thermometer; yet even in it the increasing expansibility, as the temperature rises, is perceptible in the whole range of temperature, between the freezing and boiling of water, as is well shewn in the following table, given by De Luc, according to Reaumur's scale * :—

* *Recherches*, t. i. p. 301.

Real temperature.	Corresponding points of the Merc. in the Therm.	Expansions of the Merc. at the respective temperatures.
80	80.0	5.3
75	74.7	5.3
70	69.4	5.2
65	64.2	5.2
60	59.0	5.2
55	53.8	5.1
50	48.7	5.1
45	43.6	5.0
40	38.6	5.0
35	33.6	4.9
30	28.7	4.9
25	23.8	4.9
20	18.9	4.8
15	14.1	4.8
10	9.3	4.7
5	4.6	4.6

Other fluids shew the same progressive expansibility, as their temperature rises. Dividing that part of the thermometrical scale between the freezing and boiling of water equally, De Luc ascertained, that the expansion of the following fluids in the higher division, or from 122° to 212°, is to that in the lower, or from 32° to 122°, in these proportions:

That of	quicksilver,	as 15	to 14.0
	Olive and linseed oil,	15	13.4
	Chamomile oil,	15	13.0
	Water saturated with salt,	15	11.6
	Alkohol,	15	10.9
	Water,	15	4.7*.

* *Recherches*, t. i. p. 311.

From this table it is apparent, that the rate of progression in the expansibility of different fluids is different, and the same fact is more minutely shewn in the following table of their expansions, for every 5 degrees of Reaumur's scale * ;

Mercury.	Oil of olives	Essent. oil of chamomile.	Essent. oil of thyme.	Strong spirit of wine.	Water saturated with sea-salt.	Common water.
80	80.0	80 0	80.0	80.0	80.0	80.0
5	5.4	5.3	5.7	6.2	5 9	9.0
75	74.6	74.7	74.3	73.8	74.1	71.0
5	5.2	5.2	5.5	6.0	5.7	9.0
70	69.4	69.5	68.8	67.8	68.4	62.0
5	5.0	5.2	5.3	5.9	5.8	8.5
65	64.4	64.3	63 5	61.9	62.6	53.5
5	5.1	5.2	5.2	5.7	5.5	7.7
60	59.3	59.1	58.3	56.2	57.1	45.8
5	5.1	5.2	5.0	5.5	5.4	7.3
55	54.2	53.9	53.3	50.7	51.7	38.5
5	5.0	5.1	5.0	5.4	5.1	6.5
50	49.2	48.8	48.3	45.3	46,6	32.0
5	5.2	5.2	4.9	5.1	5.4	5.9
45	44.0	43.6	43 4	40.2	41.2	26.1
5	4.8	5.0	5.0	5.1	4.9	5.6
40	39.2	38.6	38.4	35.1	36.3	20.5
5	5.0	5.0	4.9	4.8	5.0	4.6
35	34.2	33.6	33.5	30.3	31.3	15.9
5	4.9	4.9	4 9	4.7	4.8	4.7
30	29.3	28.7	28.6	25.6	26.5	11.2
5	5.0	4.9	4 8	4.6	4.6	3.9
25	24 3	23.8	23.8	21.0	21.9	7.3
5	5.0	4 9	4.8	4.5	4 6	3.2
20	19.3	18.9	19 0	16.5	17.3	4.1
5	4.9	4.8	4,8	4.3	4.5	2.5
15	14.4	14.1	14.2	12.2	12.8	1.6
5	4.9	4.8	4.8	4.3	4 4	1.4
10	9.5	9.3	9 4	7.9	8.4	0,2
5	4.8	4.7	4.7	4.0	4.2	0,6
5	4.7	4.6	4.7	3.9	4.2	0.4
5	4.7	4.6	4.7	3.9	4.2	0.4

De Luc found, that near to the boiling point of fluids, their expansibilities increase rapidly, and are

* *Recherches*, t. i. 271.

very irregular; we find, that in the greater number of fluids, there are also considerable irregularities in their changes of volume at their freezing point. Hence De Luc concluded, that the expansions of fluids would be most equable, or would correspond most strictly with the increments of their temperature, towards the middle of the range of temperature between their freezing and boiling points; and he justly inferred, that the fluid best adapted, in point of accuracy, to thermometrical purposes, is that which has the greatest range of temperature between its freezing and boiling temperatures, which gives the preference to mercury.

Since liquids thus expand in an increasing ratio as their temperature rises, we should perhaps be disposed to conclude, that a similar law is observed in the expansions of aëriform fluids, or that their expansibilities increase as their temperatures rise; and, accordingly, it appeared to be established by some experiments, particularly those already referred to, of Guyton and Prieur. While atmospheric air, in being heated from 32° to 77°, expands $\frac{1}{112.67}$, its expansion from receiving another equal increment of temperature, or in being raised from 77° to 122°, is not less than $\frac{1}{75.61}$, and from 122° to 167° $\frac{1}{52.49}$. In the other airs there were similar, and in several of them greater differences. Thus, in the expansion of nitrogen gas, it amounted to $\frac{1}{588}$ of its volume, for each degree of Reaumur's scale from 0 to 20° of that scale; from 20° to 40° it amounted to $\frac{1}{108}$; from 40° to 60°, $\frac{1}{136}$; and from 60° to 80°, more than $\frac{1}{7}$. Or the whole rate of expansions of the diffe-

rent airs, according to these experiments, is shewn in the following table *:

	From 0° to 20°.	From 20° to 40°.	From 40° to 60°.	From 60° to 80°.
Common air dilates to	$\frac{1}{12.67}$	$\frac{1}{5.61}$	$\frac{1}{2.49}$	$\left(\frac{1}{3.57}\right)$
Oxygen gas.	$\frac{1}{22.12}$	$\frac{1}{4.92}$	$\frac{1}{1.53}$	$\left(3+\frac{1}{1.73}\right)$
Nitrogen gas.	$\frac{1}{29.41}$	$\frac{1}{5.41}$	$\frac{1}{1.82}$	$5+\frac{1}{57.2}$
Hydrogen gas	$\frac{1}{11.91}$	$\frac{1}{6.92}$	$\left(\frac{1}{6.85}\right)$	$\left(\frac{1}{58.82}\right)$
Nitrous gas	$\frac{1}{15.33}$	$\frac{1}{9.00}$	$\frac{1}{3.739}$	$\left(\frac{1}{6.88}\right)$
Carbonic acid gas.	$\frac{1}{9.049}$	$\frac{1}{5.099}$	$\frac{1}{2.31}$	$\left(\frac{1}{3.69}\right)$
Ammoniacal gas.	$\frac{1}{3.58}$	$\frac{1}{1.75}$	$1+\frac{1}{1.35}$	$\left(3+\frac{1}{4.69}\right)$

There can be little doubt, however, but that these results are erroneous, and that they were obtained principally from water being present in the apparatus, which passing into vapour, at the higher temperature, would give rise to the great apparent expansion. The subject has been investigated with more care by Mr Dalton, who has found, that the expansion of aëriform fluids appears to

* Nicholson's Journal, vol. iii. p. 257.

be rather a decreasing one with regard to temperature, or from a given elevation they expand rather less at a high than at a low part of the scale. Thus with regard to atmospheric air, for "77½ degrees above 55° of Fahrenheit, the expansion was 167 parts, while for the next 77½ it was only 158 parts, and the expansion in every part of the scale seems to be a gradually diminishing one in ascending *." The same diminution appeared in the other aëriform fluids. At the same time, as Mr Dalton himself has remarked this diminution may be only apparent, and may arise from the mercurial thermometer not being a perfectly accurate measure of temperature, from mercury expanding more as the temperature is high.

The anomalous, and somewhat complicated facts which have been stated with regard to expansion may, I believe, be generalized, or the principle which connects and explains them may be pointed out.

Caloric and the attraction of cohesion are antagonist forces, the operation of either always opposing resistance to, and diminishing the effect resulting from, the operation of the other. Expansion arises from the excess of energy in the repulsive power over the force of cohesion, and from considering it under this point of view, the various phenomena connected with expansion may be explained.

Thus, in the first place, it has appeared, that the expansibility of solids is less than that of liquids, and the expansibility of liquids less than that of airs. Now, in so-

* Manchester Memoirs, vol. v. p. 599.

lids, the power of cohesion is greatest; the most effectual resistance, therefore, will be opposed in them to the operation of caloric, and hence less expansion will be produced by its introduction. In liquids the cohesion is much more weak, the expansion therefore will be proportionally greater. And in airs, as the cohesion is entirely overcome, no resistance is opposed to the expansive force of the caloric, and an enlargement of volume limited only by the pressure applied will be produced.

In different solids, the expansibility is also extremely different; and, according to the view I have stated, this may be supposed to arise from the different degrees of force with which cohesion is exerted. We have no accurate measures of this force. But if we regard the different fusibilities of bodies as affording an indication of it, we find, as has already been observed, that in general the expansibility is directly as the fusibility.

In fluids there likewise exist differences in the expansions they suffer; and there can be no doubt, that though in all of them the power of cohesion is weak, it may still be of different degrees. If we judge of these degrees from the volatility of bodies in this state, the disposition to volatility being less as the cohesion is stronger, we find also under the general point of view which experiments influenced by various circumstances must be taken, that the expansibility of liquids is in a great measure proportioned to their volatility. Hence it appears, that both in solids and liquids, the expansions produced by equal increments of temperature are less as the cohesion exerted between their particles is stronger.

But in substances existing in the aëriform state, we find no difference in expansibility as among solids and liquids, the expansions of all being alike; and this is precisely what the theory leads us to expect. Cohesion is not exerted among *them* with different degrees of force; for in all of them it is entirely overcome. No various degrees of resistance, therefore, are opposed to the operation of caloric, and hence under the same pressure, the same increase of temperature is followed in all aërial fluids by the same degree of expansion.

We have next to explain the second general fact connected with expansion, that in bodies in one state it proceeds in an increasing ratio with regard to temperature, while in others it proceeds equably, and to this the same principle may be successfully applied.

In liquids the expansibility increases as the temperature rises; the reason is, that by the introduction of caloric operating as an expansive power, and causing an increase of temperature, the force of cohesion is diminished—in proportion as the temperature rises, therefore, it becomes weaker, and opposes less resistance to the expansive energy of caloric. A greater expansion must therefore be occasioned by an equal quantity of caloric at a high than at a low temperature, because the force which opposes it is by the very increase of temperature diminished.

We find that the rate at which this expansibility varies, is different in different liquids, and even to this minute fact an application of the theory may be made; for in examining these differences, we find that the more expansible a fluid is, its expansibility by increase

of temperature increases at a higher ratio. Thus mercury, which suffers the least change of volume from any given increase of temperature, is that, the expansibility of which is most equable, or increases least as its temperature is raised.

In aëriform bodies, on the contrary, we find the expansion uniform, or it is not more from a given quantity of caloric, at a high than at a low temperature. The cause is obvious: In aërial fluids no cohesion exists to be weakened by augmentations of temperature, the resistance to the operation of caloric is just the same, under a given pressure, at a low as at a high temperature, or at both is nothing; the repulsive power of caloric ought therefore to act equally according to the quantity in which it is added; hence the expansibility ought not to be more at a high than at a low temperature. We have therefore a strict coincidence between the fact and the theoretical deduction.

It follows as a consequence of this theory, that in solids the expansibility ought to increase with the temperature. Cohesion exsists in them opposing the operation of caloric; this cohesion is weakened as the temperature is raised, and therefore an equal quantity of caloric ought to produce a greater expansion at a high than at a low temperature. At the same time, the cohesion in solids compared with liquids is so great, that the same change of temperature can by no means be supposed to produce the same difference in expansibility; and hence the ratio of increase must be much less. Solids, too, suffer so inconsiderable an expansion from even a considerable rise of temperature, that it is not

easy to ascertain the fact with accuracy. General Roy, in his experiments on the expansions of metals already quoted*, observed, that they appeared to be not equable, but progressive when tried at the temperatures of 60° 120° and 180°. Yet he seems disposed to conclude, that when the instruments are perfect, and due allowance made for the difficulty of keeping water (the medium by which the heat was applied) at a stationary temperature for any length of time, the expansions were equable. The error, however, from this cause, might have been as well on the one side as on the other, and the fact on this subject must be regarded as not ascertained. I am at present engaged in making some experiments with regard to it.

I have now to take notice of some exceptions to the law that bodies are expanded by caloric.

The most general, is that enlargement of volume which several substances suffer in passing from the fluid to the solid form. When a fluid has its temperature reduced, it contracts with more or less regularity until it reach the point at which it becomes solid. The reduction of its temperature must still be continued to produce the change of form; but at the moment that it congeals, instead of contracting, it in different instances expands with considerable force. This is remarkably the case with water; its expansion in freezing is capable of overcoming a great mechanical force. Boyle found, that by the freezing of a small portion of water, a weight of 72 lbs. was raised. The Florentine Acade-

* Philosophical Transactions, vol. lxxv.

micians made some experiments, in which a brass globe, the cavity of which was an inch in diameter, was burst by this expansive power, though, calculating from the tenacity of brass, and the thickness of the sides of the globe, it must have required a force exceeding 27,720 lbs.: and Major Williams more lately made some experiments with similar results, an iron plug $2\frac{5}{8}$ lb. weight, being projected from a bomb-shell to the distance, in one experiment, of 415 feet, with a velocity of more than 20 feet in a second, and in another experiment the shell being burst *.

From this expansion of water in freezing, the specific gravity of ice is always inferior to that of water, as is evident from its floating on the surface of water.

This expansive force, exerted in the act of freezing, has been ascribed to the extrication of the portion of air which water holds in solution, and which freezing disengages. Though this may have some share in the effect, it is far from being the sole cause; for it is found that the expansion still takes place when the water has been freed as much as possible from this air, by the air-pump. An experiment of this kind was made by Boyle †.

Mairan explained it on the supposition of a polarity in the particles of the water, or a tendency to unite by certain sides in preference to others; to arrange themselves in a certain manner, and run into right lines at determinate angles. The explanation appears

* Transactions of the Royal Society of Edinburgh, vol. ii p. 23.

† Boyle's Works, vol. ii. p. 546.

to be just. When the freezing of water is examined by the microscope, this peculiarity of arrangement can be observed, the lines shooting out from each other at an angle either of 60° or of 120°. A similar arrangement is conspicuous in a newly fallen flake of snow. The freezing of water, therefore, is a species of crystallization, and, in consequence of the arrangement it produces, vacuities are formed in the solid mass, and its volume, compared with the fluid, is enlarged.

The same phenomenon is perceived, though to a less extent, in some other substances. Iron, in becoming solid, expands, and hence the delicacy of the impression it receives from a mould. So do bismuth and antimony, and perhaps some other metals, though others, as quicksilver, conform to the more general law, and suffer contraction. In the crystallization of saline solutions by exposure to cold, expansion, from the same cause, frequently takes place; not always however, for both nitric and sulphuric acid contract considerably in congealing, though their congelation is a species of crystallization.

But a phenomenon still more singular, is exhibited by water. It expands, not only in the moment that it passes to the solid form, but before it reaches its freezing point.

Suppose we have a quantity of water at 50°, in a glass thermometer tube, in reducing its temperature it suffers diminution of volume, and does so until it arrives at about 40° of Fahrenheit's scale, but at that point the contraction ceases; and if its temperature be still farther reduced, it begins to expand, and continues expanding with an increasing ratio, until it be-

come solid. Or, if we reverse the experiment, and communicate caloric to water at 32°, instead of expanding it contracts, and continues to do so until it arrives at 48° of Fahrenheit, when it appears nearly stationary. At 42° its expansion is perceptible, and continues as its temperature ascends.

This singular phenomenon, it has been remarked by Dr Hope, seems first to have been observed by Dr Croune, towards the close of the 17th century. He announced it to the Royal Society, and even then its reality was disputed by Dr Hooke, who ascribed it merely to the contraction of the vessel in which the experiment was made. So little attention was afterwards paid to the observation, that it seems nearly to have been forgotten, until again observed by Mairan. De Luc was the first who investigated it with any precision *. He fixed the point at which the expansion commences, at 41° of Fahrenheit; and he supposed the expansion from that point, either towards a higher or lower temperature, to be the same; so that the density of water at 50° and at 32° is alike.

It was observed by Sir Charles Blagden, that if, by avoiding agitation, the freezing of water at 32° was prevented, and it was cooled to 21° or 22°, the contraction still continued to proceed, and in an increasing ratio; or, if its freezing point was reduced, by dissolving certain salts in it, the expansion began at about the same distance from the point at which such a solution does freeze, as that which pure water ob-

* *Recherches sur les Modific. de l'Atmosph.* t. i. p. 225, &c.

serves *. At a subsequent period, he endeavoured to determine the difference of density in water at these temperatures in a different mode. He weighed distilled water at 40°, in a bottle filled with it, and the weight of the water he found to amount to 2967.34 grains, while, when filled with distilled water at 35°, the water weighed only 2967.03. At the same time he endeavoured, by calculation, from the known expansibility of glass, to make the due allowance for the difference in the volume of the bottle from the difference of temperature; and with this correction he states the specific gravity of water at 35° to that at 40°, as 1.00087 to 1.00091, that at 60° being 1.00000 †. From the very different expansibilities of glass, however, and the difficulty of ascertaining the data accurately, much confidence cannot be placed in this calculation.

Mr Dalton likewise made this the subject of experiment. He fixed the maximum of density at $42\frac{1}{2}^{\circ}$ of Fahrenheit, by the mercurial thermometer. From 41° to 44° the expansion is so inconsiderable as to be barely perceptible; from either of them it proceeds in an increasing ratio, and, in the reduction of temperature from 41°, when the fluid has arrived at 32°, the expansion it has suffered amounts to about $\frac{1}{100}$th part of the whole expansion from $42\frac{1}{2}^{\circ}$ to 212°. Mr Dalton confirmed the observation of De Luc, that the expansion for any number of degrees, either above or below the point at which it commences, is the same;

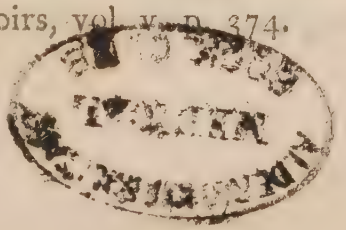
* Philosophical Transactions, vol. lxxviii.

† Ibid. vol. lxxx. p. 333.

so that, taking this point at 42.5, the density of water must be the same at 32° and at 53° ; or, supposing the stationary point to be 40°, water at 32° will have the same density as water at 48°. By more strict examination of the fact, he has since found that the expansion for the degrees below the stationary point, appears somewhat greater than for a corresponding number of degrees above that point, 29 degrees below affording the same expansion as 33 above, though this may be only an apparent difference from the error attached to the common mercurial scale. He confirmed also the observation of Blagden, that the expansion continues to proceed below 32° when the water is cooled beneath that without freezing, and that it increased at a very high ratio. He succeeded in cooling it so far, that in the tube in which he made the experiment, the water from expansion had risen as high as the point to which it would have been raised had it been heated to 75°. Its real temperature must then have been 10°. On freezing, it darted suddenly up to 128° *.

Mr Dalton has, in consequence of later investigations, changed his opinion on this subject, and considered this anomaly exhibited by water as apparent, not real, and has explained it in the same manner as Hooke did, from the contraction of the vessel in which the experiment is made. The usual mode of making the experiment, is, to put a quantity of water into a ball with a cylindrical stem, of narrow bore, similar to a thermometer, and to cool it, the expansion of the

* Manchester Memoirs, vol. v. p. 374.



water, in cooling, being measured by its ascent in the tube. It is evident, that in this experiment the glass-ball being cooled, must contract, and must contribute in part at least to the rise of the fluid. By Mr Dalton it is regarded as the sole cause; and the same opinion appears to have been adopted by several chemists.

It must naturally occur as an objection to this opinion, that did the apparent expansion of the water arise from the contraction of the glass ball, the same phenomenon ought to be exhibited by other fluids; and the question might also be put, why should it appear only at the part of the thermometrical scale at which it does? Both these objections, however, may be answered. The reason why the apparent expansion is exhibited only by water, may be said to be that it is the fluid in which the changes of volume at that temperature are least considerable. Its contractions from diminution of temperature are so small, as to be inferior even to the contractions of glass; hence apparent expansion; while in other fluids, the contractions being more considerable, they are not exceeded, or even equalled by those of the instrument, and, though no doubt lessened by that cause, are still apparent. The reason why the apparent expansion of water takes place only as it approaches its freezing point, is, that its expansibility is in an increasing ratio with regard to temperature. The farther it is cooled the less considerable are its contractions from given decrements of temperature; and continuing thus to diminish, they are at length inferior to the contractions

of the glass, and from the point at which this happens, the apparent expansion must begin.

Thus is explained this singular appearance. Water, in the reduction of its temperature to the point at which it becomes solid, conforms to the general law, and suffers contraction; but this contraction becoming less as it approaches to its freezing point, is at length exceeded by the contraction of the vessel, and then apparent expansion of the fluid must take place.

So far the opinion appears not improbable; and the experiments by which Mr Dalton endeavoured to establish it, are far from being inconclusive. It is obvious, that if the explanation which refers the rise of the fluid in the tube, to the contraction of the vessel, be just, that rise must be different in its extent, and in the point at which it commences in vessels constructed of different kinds of materials; for the expansion of any substance is peculiar to itself, and different from every other; that of glass is not the same as that of any metal; their contractions from cold must therefore be different, and their effect of course, in pressing on a contained fluid, must be unequal.

Proceeding on this idea, Mr Dalton repeated the experiments in vessels of earthen ware, and of different metallic substances, and compared the results with the experiment made in glass. In all they varied, or the point of maximum density, instead of being uniform, or nearly so, was different in each. The following table will shew the differences:

	Water lowest.	Water the same height.
Brown earthen ware, No. 1,	at 36°	at 32° and 40°
Brown earthen ware, No. 2,	38	34 and 44
Queen's ware,	40	32 and 48
Flint glass,	41½	32 and 51
Iron, thin plate,	42½	32 and 53
Copper,	45½	32 and 59
Brass,	46	32 and 60
Pewter,	46	32 and 60
Lead,	49½	32 and 67 *

It is no doubt true, that the containing vessel must always influence the result in experiments of this nature, or the observed expansion cannot be the real expansion; and the point of greatest density, or that at which the expansion commences, must be always somewhat lower than it appears. Suppose the water to be possessed of this anomalous property, when cooled in a ball of any kind of matter, to which a cylindrical stem is attached, it will ascend in the stem from its expansion; but this ascent will be rendered greater, and may even commence sooner, from the contraction which the ball suffers at the same time; and hence the observed expansion, must in part arise from the one cause, in part from the other, and will be greatest in a ball made of a substance which expands much from a change of temperature, and, *vice versâ*, will be least in one which suffers little expansion. The in-

* Nicholson's Journal, vol. x. p. 95.

fluence of this is easily traced in the preceding experiments. Lead is the metal which suffers the greatest expansion, as appears from the table of Ellicot already given; hence, in a ball made of lead, the point of greatest density is raised highest in the thermometrical scale, or appears at $49°\frac{1}{2}$. Brown earthen-ware, on the contrary, it appears from Mr Dalton's own experiments, is very much inferior in expansibility to the metals, as was shewn by plunging a thermometer constructed with it in warm water, when, from the expansion of the ball, the liquor in the stem instantly sunk for a moment; but in the instrument of earthen-ware, this was only 0.2, while in lead it was 1.5. Still from these facts the conclusion cannot be drawn, that the contraction of the vessel is the sole cause of the ascent of the fluid. On the contrary, as the expansibility of earthen-ware is so inconsiderable, it may be inferred, that in the reduction of its temperature, from 40° to 32°, the contraction is so small, as to contribute very little to the apparent expansion of the water in the preceding experiments; and that these prove, therefore, without searching for any other fallacy, nothing more, than that the point of greatest density is lower than had been supposed, and is perhaps a little below 36°. Another source of fallacy may perhaps exist in the porosity of the earthen-ware.

The question as to the existence of this anomaly in water, has since, however, been made the subject of investigation by Dr Hope, and its reality fully demonstrated, by experiments conducted in a manner

altogether different from the preceding, and free from the objections to which they are liable.

It occurred to Dr Hope, that if water did expand in the reduction of its temperature from 40°, the expansion might be discovered by the change of place which would happen in a column of water, while cooling from 40° to 32°, or heating from 32° to 40°, as the water towards 32° would necessarily rise in either case towards the surface.

A cylindrical glass jar, therefore, $8\frac{1}{2}$ inches deep, and $4\frac{1}{2}$ inches in diameter, was filled with water at 32°, a thermometer being suspended in it, nearly in the axis, so as to have its bulb distant about half an inch from the bottom; and another, in a similar position, at the same distance from the surface of the fluid. The jar being exposed to the air of a room at the temperature of 60° caloric, would be communicated to the water. Did the water expand from this communication, it is obvious, that it must rise towards the surface, and that while any inequality of temperature existed in the mass, the thermometer there must indicate a higher temperature than the thermometer near to the bottom; while if it contracts from the addition of caloric, the reverse of this must happen. The result of the experiment was, that in the progression of temperature up to 38°, the thermometer at the bottom was always one degree at least higher than that at the surface, a sufficient proof that the water, as its temperature rose from 32°, had become more dense.

By cooling water to 32°, a similar result was obtained; the thermometer at the bottom still remaining higher than that at the surface. And this experiment was conducted, so as to shew clearly the accuracy of the method; for when the water was taken of the temperature of 53°, in cooling to 40°, the colder water is found at the bottom; the difference between its temperature, and the temperature of that at the surface, amounting even to 7 or 8 degrees. When the fluid at the bottom has attained 40°, it remains at that until the whole reaches that point; and then the progress of the cooling begins to be reversed, or the colder fluid now is found at the surface, while that at the bottom is 4 degrees warmer.

These experiments were varied, by communicating or abstracting caloric, not to or from the entire mass of fluid, but at the surface, the middle, or the bottom of the vessel. The results were thus rendered still more striking and conclusive. Above 40°, the warmer part of the fluid always is at the top of the vessel, while the colder is found at the bottom. Below 40° this arrangement is reversed, the warmer part appears to be of greater density, and descends; the colder, being more expanded, is elevated to the surface, where it remains. In communicating heat or cold to the middle of the jar, the determination of these currents is well displayed. The whole experiments establish the conclusion, that the point of greatest density in water is not at its freezing point, but a considerable number of degrees above it; and

that as it approaches to that point, it suffers expansion *.

Mr Dalton has indeed since admitted, that the point at which water is of the greatest density is not at 32°, but is some degrees above it, or, as he supposes, about 36° ; and he has employed a good deal of reasoning to shew, that from Dr Hope's experiments it cannot be inferred to be higher than this †. Whatever may be the exact point at which the expansion commences, the important result is at least established, that the anomaly with regard to water exists ; and it must be difficult to ascertain it with perfect precision, for the expansion being an increasing one, wherever it commences, it must in the first stages be extremely inconsiderable. A variation, however, which I made in Dr Hope's experiment, may perhaps give a method which will determine it with more accuracy than any other. It occurred to me, that it might be satisfactory to observe directly the changes of place in the column of fluid submitted to experiment, instead of inferring them from the changes of temperature in the thermometer. Having prepared, therefore, a dilute solution of litmus, I divided it into two portions, one of which was tinged red by the smallest possible quantity of sulphuric acid ; to the other a drop or two of solution of potassa was added, in order to preserve

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* Transactions of the Royal Society of Edinburgh, vol. v. p. 379.

† Nicholson's Journal, vol. xiii. p. 377. ; and vol. xiv. p. 128.

the specific gravity the same. This was so well attained, that by means of a filtre the two fluids could be introduced into a jar, so that the one stood over the other indiscriminately, according to the order in which they were introduced. Having prepared a column of fluid of this kind, the purple-coloured infusion, for example, being placed in a glass jar, 2 inches in diameter, at the bottom to the height of 4 inches, and the crimson-coloured infusion above to the height of 1 inch; the temperature of both 40° ; on applying, by a sliding cup, a freezing mixture to the top, the temperature of the red liquor was reduced to 32° ; but it did not descend ; and at the end of half an hour, the line of distinction was perfectly defined, spiculæ of ice shot from it, and the temperature of the liquor towards the bottom was shewn by a thermometer to be 39°. Here, therefore, the density of the liquor had not increased. On putting the crimson-coloured infusion at the bottom to the height of $1\frac{1}{4}$ inch, and the blue above it to the height of 4 inches, when a freezing mixture was placed around the red, the temperature of the whole being 40°, in 3 minutes it began to ascend in streaks, and in $7\frac{1}{2}$ minutes the colour of the whole was uniform, affording a very clear proof of the inferior density of the water at the lower temperature.

These experiments having been made prior to the publication of Mr. Dalton's last observations, it did not occur to me to ascertain exactly at what point the expansion commenced. But it is obvious, that this kind of experiment is well calculated to determine

this, since, if a jar be filled with the two liquors, as above described, having the bulb of a delicate thermometer in the one liquor, and that of another equally sensible in the other, and cold be applied to the under liquor, we shall be able to discover the precise temperature at which it is inferior in density to the liquor above; the temperature of which will, at the same time, be also indicated, and thus the point of greatest density may be discovered. With this view, I shall take an opportunity of performing the experiment.

Considering the fact as established, that water expands in the reduction of its temperature, for some degrees before it passes into the solid state, we must be disposed to inquire if any cause can be assigned for this anomaly. The explanation stated by Sir Charles Blagden, has been generally acquiesced in. It seemed not improbable, that that peculiar exertion of the attraction of cohesion, which gives rise to the arrangement of the particles, so as to unite them in symmetrical forms, may commence some degrees before the point at which it becomes sufficiently efficacious over the repulsive power of caloric to produce solidity. This arrangement may produce enlargement of volume, which shall exceed even the contractions that would result from the abstraction of caloric.

It might be supposed, that were this explanation just, the water should suffer some diminution of its fluidity, or some increase of tenacity, which, from an experiment Dr Hope made with the gravimeter, he infers, does not happen. The experiment, however,

as Dr Hope himself has remarked, is liable to some fallacy, from the operation of temperature on the instrument, the exact amount of which it is not very easy to estimate. Since cohesion exists in fluids, it seems scarcely to be doubted, but that its force will be increased by diminution of temperature; and the conjecture that it is, appears to be established by an observation made by Mr Leslie, that from this cause water drops from a small tube with six times more velocity when it is near its boiling point than when it is on the verge of congellation *. It might be said, that here also there is a source of fallacy, the extent of which at least it would be necessary to ascertain, before any strict conclusion can be drawn; the difference in the diameter of the aperture, at the different temperatures at which the experiment was made. At 212° this must, from the expansion, be greater than at a low temperature; and hence the water must, at the former temperature, drop more quickly. There is reason to believe, however, from the known expansibility of glass, that this is not sufficient to account for the difference; and the general deduction from theory may perhaps be regarded as sufficiently probable, that the cohesion of fluids must vary with temperature, though the extent of the variations cannot well be determined.

There appears sufficient reason to believe, that, in other fluids, which expand in the act of congealing,

* Philosophical Magazine, vol. xiv. p. 204.

this expansion takes place, as it does in water, through a certain range of temperature above the point of congelation. Some observations made by Mr Mushet seem, in particular, to shew that this is the case with iron. If on pieces of iron, melted iron be poured, they will immediately float, and expose a considerable portion of their bulk above the surface of the liquid iron, a sufficient proof of the greater density of iron in its fluid than in its solid state. But this buoyancy diminishes; and as the pieces of metal approach more and more to the state of fusion, they gradually sink, till they disappear entirely under the surface *; from which it may be inferred, that, in proportion as the temperature of the fluid iron is reduced, its density is diminished.

I have to state still one other exception to the law of expansion from caloric,—that observed in the different natural clays and the pure earth, argil, which predominates in their composition. These, instead of expanding by increase of temperature, diminish in volume. It is on this property of clay, as I have already stated, Mr Wedgwood constructed his pyrometer; and he has ascertained the principal facts that have been observed with regard to it.

The contraction is not considerable and is irregular at temperatures below ignition, and seems to proceed principally from dissipation of moisture, and expulsion of aërial matter. At the approach to ignition, a

* Philosophical Magazine, vol. xviii. p. 8.

slight degree of enlargement of volume is even observed, and is accompanied with an extrication of air; but, at a full red heat, contraction again takes place, and from this point proceeds as the temperature is raised, until the heat is sufficiently intense to produce complete vitrification; when that change takes place, which happens at different degrees of heat in different varieties of clay, the property is least. Through this stage the clay still remains porous, and is bibulous. At the commencement of vitrescence, the mass expands, but, by urging the heat, it becomes fluid, is converted into a slag, and is contracted into less volume than the clay occupied in any of its preceding states.

It is difficult to assign the cause of this anomalous property in these substances. As the contraction is permanent, or remains when the clay has become cold, it might be supposed to depend on some change of composition. It has been supposed to be owing to the expulsion of some volatile matter, particularly of water, which clays imbibe with avidity, and retain with force, and which may be gradually expelled, as the heat rises in intensity. But this supposition seems to be refuted, by the fact ascertained by Mr Wedgwood, that his pyrometrical pieces, at very high temperatutes, sustained no diminution of weight, though they continued to contract. At a low red heat, it has been already stated, a disengagement of aërial matter, apparently a mixture of common air and carbonic acid, takes place; from that to a strong red heat there is a loss of weight, amounting to about 2 parts in the 100. But past this there is no further loss. This has been

ascertained also by Saussure. The pyrometrical pieces he employed lost 2½ grains by heating to the 29th degree of the scale; but beyond that, to the 170th, they lost no weight, though diminished one fourth in volume *

Perhaps it may be ascribed to the exertion of the attraction of cohesion being favoured by the operation of caloric, so as to admit of a closer aggregation. The clay may be conceived of, as consisting of small masses, imperfectly united, and having between them many interstices; by the high temperature, the more perfect union of their particles may be favoured, from which diminution of volume may arise. What at least adds to the probability of some explanation of this kind is, that the clay acquires a great degree of hardness, proportioned to the heat to which it has been exposed; and that, at length, it is with difficulty acted on by substances, in which, in its natural state, it is easily soluble. Sir James Hall, in his experiments on heat modified by compression, observed, that chalk suffers changes somewhat analagous to these. When a solid piece of chalk which had been previously measured in the gage of Wedgwood's pyrometer, was submitted to heat, under compression, its contraction was three times greater than that of the pyrometer pieces in the same temperature; it lost almost entirely its power of imbibing water, and acquired a great additional specific gravity, proving, as Sir James has remarked, the approach of the particles during their consolidation †.

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* Philosophical Magazine, vol. x. p. 155.

† Edin. Philosoph. Trans. vol. vi.

With the exceptions which have now been stated, all bodies which have not their composition or texture permanently changed by caloric, suffer expansion from its introduction, and contract again when it is withdrawn.

FLUIDITY.

The second general effect produced upon bodies by the entrance of caloric, is Fluidity, or their conversion to the liquid state.

It has been shewn, that when caloric is introduced into a body, the volume is augmented, or the particles are separated to greater distances from each other. This augmentation of volume continues to go on in proportion to the increase of temperature until the particles are separated to such distances as to be easily moveable in every direction. This constitutes the fluid form. By a reduction of temperature, the particles again approach, when, within certain distances from each other, they coalesce, and the fluid is brought back to the solid state.

These different changes of form depend on the relative action of caloric, and of the force of cohesion. By the mutual attraction which subsits between the particles of bodies, they are made to approach, and are united, so as to form solid masses. Were this power only exerted, all bodies would appear under this form, their particles would be in actual contact, and every mass would be equally dense and hard. But its force is counteracted by the repulsive agency of caloric, by which the particles are separated to distances at which the attraction ceases to operate with much force.

When the one force predominates, the body appears in the solid state; when the other prevails, it passes into the fluid form.

Yet fluidity is not to be regarded as consisting merely in the weak cohesion existing among the particles, in consequence of the distance at which they are placed by the action of caloric, but also on a new arrangement accompanying this, or produced by it, into which the particles enter. Cohesion still exists in the fluid, and it is not even easy to determine to what extent; and that a change in the position of the particles of the body, so that they assume one which is determinate, takes place, is proved by the facts which have been stated with regard to the contraction some substances experience in becoming fluid,—facts inconsistent with the supposition, that fluidity depends merely on a weaker cohesion between the particles, from the greater distances at which they are placed. The view which has been given of this subject by Professor Robison, appears to be extremely just *. He remarked, that to explain the mobility of a fluid, or the facility with which its parts are separated, it is necessary to suppose only that the action of its particles, whatever it may be, is equal in every direction, at the same distance; as if there exist this equality, it can require no force to move an adjacent particle from one situation to another, nor any force to keep the particle in its new situation with regard to the rest of the fluid.

* Black's Lectures, vol. i. p. 517.

And still the attraction exerted between the particles, provided it be equal, may be strong. On the other hand, in a solid, the particles must attract more strongly in one direction than in another; hence a particular situation of each particle must be assumed, and a force, more or less great, will be requisite to change its position. It follows, therefore, from this view, and from the preceding facts, that fluidity arises not merely from the weakness of cohesion between the particles, but also from the change in the mode in which they attract each other. But this, at the same time, no doubt arises from the expansive energy of caloric, which, in separating the particles to certain distances, gives rise to this modification in their mutual action; whence they assume different positions, and attract with a different but equal force.

From this view of fluidity, as depending on the action of caloric increasing the distance, and ultimately changing the direction in which attraction is exerted, it follows, that it is to be regarded as not essential to any species of matter, but as depending on the presence of caloric. The solid state is the natural state of every body; and there can be no doubt but that every fluid is capable of being rendered solid by the necessary reduction of temperature. Every known liquid, with the exception of alkohol, has indeed been already reduced to the solid state; and the difference in the degrees at which different bodies suffer this change of form, depends entirely on the relative force of cohesion, by which their particles are held together. Where that force is weak, the fusion may take place at a very low tempe-

rature; and such a body will always be met with in the fluid form, unless in extreme colds. Ice melts at 32° of Fahrenheit's scale; and therefore, at all temperatures superior to this, it exists in the state of water; mercury is always fluid at any temperature higher than 40° below o of Fahrenheit: but beneath these points they become solid; nor can any of them be considered as more naturally fluid than another.

There is also no solid but what may be rendered fluid by the due increase of temperature, though some demand a very great rise compared with others. Tin, the most fusible of the metals, melts at 442° of Fahrenheit, while platina cannot be melted in the strongest heat a furnace can raise. Silver melts at 1000°, gold at 1301°, and iron at 3000°. The only substances that have not been fused are the pure earths; but when mixed together these melt readily; and even separately the greater number of them have been fused by the intense heats which the researches of modern chemistry have enabled us to excite.

In common language, those bodies which are fluid at the medium temperature of the globe, are said to be frozen or congealed when they are brought to the solid state; and those, again, which are solid at that temperature, when they are rendered fluid by an addition of caloric, are said to be melted or fused. The changes of form, however, are precisely the same; and water is as much to be considered as melted ice, as lead or iron when it is in the fluid state, is the melted metal. In a general table of the scale of temperature, to be given

at the end of the history of caloric, will be found the temperatures at which a number of bodies suffer this change of form; or the melting points of those found usually solid, and the freezing points of those which usually exist as fluids.

To guard against mistake, it may be observed, that there are many substances which we cannot melt; such are the greater part of those belonging to the animal or vegetable kingdom. A piece of wood, for instance, cannot be brought into a fluid state by any application of heat. But the reason of this is, that such bodies suffer a chemical decomposition at a temperature lower than that which would be necessary to fuse them. They are compounds; and, by the agency of caloric, the balance of attraction between their component principles is broken, and they pass into new combinations. It is thus that a piece of wood, instead of being fused by heat, is converted into water, an acid liquor, and several other new products. But such cases furnish no just exceptions to the universality of this effect of caloric.

Of the fusion of substances which, from the decomposition they suffered when heated, appeared infusible, we have a striking example in the late experiments of Sir James Hall. By the application of a strong pressure, so as to prevent the decomposition arising from the separation, by heat, of aërial or volatile ingredients, he succeeded in fusing marble, limestone or chalk, and likewise coal, which, by exposure to heat, without this management, could not be melted.

These experiments, too, so far establish the general and important principle with regard to fluidity, that when an elastic body, or one which, in its insulated state, is aërial, is combined with a solid, if its escape is prevented by sufficient pressure, it renders the solid fusible at a lower temperature. Lime, in its pure state, is not melted by the most intense heat, at least which a furnace can raise, but, when combined with carbonic acid, it is melted at a temperature, according to Sir James Hall's experiments, not greater than 25° of Wedgwood, the escape of the carbonic acid being prevented by the necessary pressure. The aërial ingredient seems to share its facility of being expanded by caloric with the solid, and thus to increase the fusibility of the latter, and the whole accords well with the view given by Berthollet, of the properties of a compound being the modified properties of its constituent parts.

There is a remarkable difference between expansion and fluidity, in the manner in which they are effected. Expansion is produced gradually, there being as many degrees of it as there are degrees of temperature, while fluidity is in general sudden, and always takes place at a precise temperature. If the body be within even one degree of its melting point, it still preserves its solid form, and when that degree of caloric is communicated to it, it immediately becomes fluid. There are some substances, however, which become soft before they pass into the state of liquids, as those of an unctuous nature. Mr Nicholson has remarked, that the same thing is observable in some of the metals. In the solder of the pewterers, for example, the interval between

the commencement of crystallization and the solidification of the whole mass, is not less than 40 degrees *. Even in those substances which appear to suffer the change of form most suddenly, there is probably a gradation in the force of cohesion. The experiment of Mr Leslie, to shew the difference in the state of cohesion near to the freezing and boiling points of water, has been already stated.

In the reduction of fluids to the state of solids, there are some circumstances which have an influence in producing the change, independent of the mere abstraction of caloric. When ice, for example, is raised to the temperature of 32° of Fahrenheit, it invariably melts, nor is it possible to raise its temperature one degree higher, as any addition of caloric only serves to melt it more rapidly, until the whole mass is resolved into water. But this water may be cooled below 32°, without being converted into ice; it may be cooled without difficulty to 27° or 25°, with care even to 23°; and Blagden succeeded in reducing the temperature of water which had been made to boil strongly, so as to expel the air, to 21° of Fahrenheit, or 11 degrees below the melting point of ice. De Luc cooled it 6 or 7 degrees lower, and Mr Dalton has brought it so low as 5° of Fahrenheit without freezing.

Different circumstances thus influence the change of form besides temperature. The most general in its action is agitation. In cooling the water below 32°,

* Journal, vol. xii. p. 362.

to prevent freezing it must be done slowly, and with perfect rest. If agitation be not guarded against, it either freezes at 32°, or if we have succeeded in cooling it below that, agitation instantly causes it to freeze, and the temperature immediately rises to the freezing point. This was observed by Mairan. Blagden, who investigated this subject by experiment, remarked, that the kind of agitation which favours freezing is rather that which occasions a vibration among its particles than that which agitates the mass: hence striking the body of the vessel containing the cooled water against a hard body would produce instant congelation, when agitating it in the hand would not have the same effect.

Water which has been deprived of air by boiling, or any other means, it has been supposed, can bear a reduction of temperature without freezing better than the purest water in which air is contained. The reverse of this, however, was established by Dr Black. He exposed equal quantities of water unboiled, and water which had been boiled for four hours, to a cold atmosphere, and found that ice was always formed first in the boiled water, and that frequently when ice was on its surface the other remained liquid, though the moment it was agitated spiculæ of ice formed, proving that it had been cooled below 32°. Hence, he remarks, the reason of the practice in India, of boiling water intended to be employed to obtain ice. Dr Black supposes this peculiarity in boiled water to arise from the circumstance that its air having been expelled, when exposed to the atmosphere, it again absorbs it;

and this absorption may occasion a slight motion among the particles at its surface, by which the congelation may be accelerated *.

The intermixture of any particles that impair the transparency of the fluid have a similar effect; so that, when abundant, it cannot be cooled two degrees below 32° without freezing.

The circumstance, however, which, with most certainty, determines the congelation of water, is the introduction of the smallest particle of ice or snow; crystals instantly shoot through the liquor from the spot the ice touches, until the whole surface is frozen. The effect of this is well illustrated in a experiment of Sir Charles Blagden's. In a calm day, when the temperature of the atmosphere was about 20°, two vessels with distilled water were exposed to the atmosphere; one of them was slightly covered with paper; the other was left open; the former bore to be cooled many degrees below the freezing point, while a crust of ice always formed on the surface of the other, before the thermometer immersed in the middle of it came to the freezing point. This phenomenon, which had been before observed, he ascribes to frozen particles which at that temperature float in the atmosphere, and which, when they touch the cooled surface of the water, instantly cause it to freeze. Oil poured on the surface of water prevents it from

* Philosophical Transactions, vol. lxv. p. 124.

freezing so readily,—an effect evidently to be ascribed to its preventing the influence of this cause.

The phenomena now stated have generally been explained on the principle, that the freezing of a fluid, such as water, is a species of crystallization, in which the particles are peculiarly arranged; this arrangement of them in the state of ice being different from that which exists among them in a state of fluidity. The existence of such a polarity, or disposition to unite by certain surfaces in preference to others, seems to be proved by the lines of ice shooting out at certain angles, and by the transition of form being accompanied with an enlargement of volume. It affords a satisfactory solution of the operation of the different circumstances which influence the transition. When the fluid is cooled, its particles are made to approximate; but the surfaces presented to each other may not be those disposed to unite. *Agitation*, by the various motions impressed on the particles, may occasion some of them to pass into a more advantageous position, or cause them to approach nearer to each other; and these effects are more likely to happen from an internal agitation than from a general motion of the whole mass. Extraneous substances, besides serving as points from which a degree of attraction may be exerted, may likewise, by various chances attending their floating in the water, throw the particles into favourable situations. Lastly, the influence of a particle of ice is evidently to be ascribed to the attraction it exerts to the contiguous particle of water, an effect which, when it is sufficiently energetic to

cause the crystallization to commence, will quickly be extended through the whole mass *.

Other fluids exhibit the same phenomenon. Mr Macnab found, that nitrous acid might be cooled from 30° to 40° below its usual freezing point; and a similar observation has been made on sulphuric acid and on mercury. A very decisive proof of it is, that they can be cooled considerably without congealing; but the moment their congelation commences, their temperature rises a number of degrees. Blagden found, that the same thing happened in many saline solutions. The solution of a salt in water generally lowered its freezing point, or enabled it to bear a greater reduction of temperature without freezing. But, in such cases, the property of bearing reduction of temperature a number of degrees below the point of congelation which it did observe, still remained. In other words, these substances dissolved in water do not take away its property of being cooled below its point of congelation, though, by depressing that point, they alter the degree of cold at which the property commences. By dissolving sea-salt, for example, in water, its freezing point is reduced to 16°, but it can with care be cooled to 9° without freezing; and a solution of nitre, the freezing point of which was 27°, could be cooled to 16°. These facts admit of a similar explanation.

During liquefaction, a quantity of caloric is absorb-

* Philosophical Transactions, vol. lxxviii. p. 141.

ed by the fluid, which does not augment its temperature; and when it returns to the solid state, this caloric is again given out, and rendered sensible. This is a chemical phenomenon of the first importance, but it will be considered with more advantage in a subsequent section.

VAPORIZATION.

When a body has been rendered fluid by caloric, by a farther rise of temperature, the fluid is expanded in the same manner as when it existed in the state of solidity. This expansion continuing to increase, as the temperature is raised, the particles of the fluid are at length separated to such distances that a change of form again takes place; the attraction of cohesion is overcome, a repulsive or elastic power is acquired, and the body becomes rare and invisible, or passes into the aëriform state. This is the third general effect of caloric. It is properly termed Vaporization.

Examples of this change of form are sufficiently familiar. When water is heated to 212° of Fahrenheit it begins to boil. This ebullition is nothing but the conversion of the fluid into vapour; that part of it which is at the bottom of the vessel receiving the caloric immediately from the fire, is quickly converted into vapour, and rising through the fluid produces the appearance of boiling. In a certain time the whole of the fluid will be found to be dissipated under this form. Other fluids, as alkohol, or ether, or a number of solids, as sulphur, camphor, &c. may be made to suffer the same change.

This process of vaporization has been distinguished from another, in which a body likewise escapes under an invisible elastic form, that of Evaporation. When water, for example, is exposed to atmospheric air, the air is conceived to attract part of it, or dissolve it, and the weight of the water is of course diminished, until it entirely disappears. A number of other bodies suffer the same change, from a similar cause. This is termed Spontaneous Evaporation. It has been regarded as the solution of a body, solid or liquid, in an aërial fluid. Vaporization, again, is the conversion of a body into an invisible elastic vapour, by the operation of caloric alone.

This invisible elastic form, into which many substances are brought by the agency of this power, is termed the gaseous or aëriform state; and when existing in it, they are named Vapours, Airs, or Gases. The two latter terms, Air and Gas, are perfectly synonymous; they are applied to denote those bodies which exist in this invisible elastic state, and which by no reduction of temperature we can command, can be reduced to the fluid or solid form. Vapours, again, are easily condensible; but while they exist in the state of vapours, they possess the same common mechanical properties as airs.

The distinguishing property of bodies existing in the aëriform state, is elasticity, or the capability of being reduced into a smaller volume by pressure, and of expanding again when that pressure is removed. All the airs and vapours are possessed of this property, and it is nearly peculiar to them; for though

there are some experiments which seem to prove, that water and some other fluids are not only compressible, but also elastic, yet it is in so inconsiderable a degree, as to be scarcely perceptible; while, on the contrary, it is possessed so remarkably by all the gases, that it is properly stated as their most distinguishing property.

The compressibility of any of these bodies is obvious, even on a very moderate pressure. The weight of a few inches of mercury is sufficient to reduce the volume of atmospheric air, or any other gas, very perceptibly. By a strong pressure, atmospheric air, it has been calculated, has been reduced to the 128th part of its volume. By mere compression, the vapours can be reduced to the fluid state.

Their elasticity is exerted with very great force. If any fluid, such as water, alkohol, or mercury, be heated in a vessel from which the vapours cannot escape, the vessel will soon be burst, though made of metal, and of considerable thickness. The elasticity of watery vapour is applied with great force, and to the most important practical purposes, in the steam-engine, a machine in which it is the sole spring of motion, productive of immense power.

The elasticity of the gases is greatly augmented by every increase of temperature. It has been already stated, that the volume of atmospheric air is increased by this cause in the proportion of $\frac{1}{480}$th part of its bulk, for each degree of Fahrenheit's scale, and the elasticity of watery vapour is nearly doubled by every 30 degrees of Fahrenheit above 212°.

2. Extreme rarity is another property, distinguishing bodies in this form. Water, for example, when it has assumed the state of vapour, occupies nearly 1800 times the space it did in the liquid state. This rarity is so great, that their particles are perfectly invisible; a glass vessel, filled with any air or vapour, being as transparent as if it contained no matter. When the vapours are condensing, they become opaque; but this is owing to a part having already assumed the fluid form, and being diffused through the remaining vapour.

3. It is scarcely necessary to add, that gravity is a property possessed by all the vapours and gases, since they consist of solid matter, brought into this form by caloric. The discovery of the weight and pressure of the atmosphere, was the commencement of the successful modern researches into the properties of the elastic fluids.

The point at which bodies pass into the aëriform state is very various. Some assume it at so low a temperature, that even the greatest cold that has been produced, is insufficient to reduce them to the fluid form. Others, as ether, alkohol, water, mercury, sulphur, and many others, are convertible into vapour by a moderate increase of temperature; ether, for example, at 104°, alkohol at 175°, water at 212°, quicksilver at 672°. Of course, these are easily reduced to the state of fluidity; while there is a third class of bodies, consisting of the metals and earths, which are not converted into vapour but by the most intense heat; there are even some of them which have

not suffered this change. These are termed Fixed, in contradistinction to those which are volatile or easily convertible into vapour; but the term is merely relative, since there can be no doubt but that even these bodies are volatile, though it may be at a higher temperature than we have been able to produce.

This difference in the degree of temperature, at which bodies assume the aërial form, has given rise to the distinction I have already noticed, as established in chemical language, between vapours and airs or gases. Different fluids, at a certain temperature, assume the gaseous form, that is, they acquire elasticity, are rarified so far as to become invisible, and are so light as to ascend in the atmosphere. While in that state, they are compressed by pressure, and expand when that pressure is removed, providing their temperature be kept up; but as soon as their temperature is reduced to a point lower than that at which they were converted into the state of vapour, they return to the fluid form. Such bodies existing in this state of elasticity are termed Vapours.

There is, however, another class of bodies likewise invisible, compressible and elastic, which differ from the former, in being not reducible by mere cold or pressure to the fluid or solid state. These, therefore, are termed Airs or Gases, and are distinguished by the property of permanent elasticity. Atmospheric air is one of these, and there are a number of others, distinguished from each other by peculiar chemical properties.

The same opinion has been entertained of these

airs, that was formed respecting those bodies which were always found fluid. Their aëriform state has been considered as natural or essential to them. But modern chemistry has sufficiently demonstrated, that they owe their form to the presence of caloric, and that could this be sufficiently abstracted, they would, like the mere vapours, be reduced, first to the fluid, and then to the solid state.

This important proposition, though even in the present day sometimes objected to as an hypothesis, is sufficiently established. It is rendered in the highest degree probable, from the general consideration of the agency of caloric; which converts solids into fluids, and fluids into vapours. These vapours possess all the mechanical properties of airs, and it is demonstrable, that if the bodies existing in the state of vapour, had assumed that state at a lower temperature, they would have possessed the only distinguishing property of airs, permanent elasticity. If water, for instance, instead of requiring a temperature of 212°, to convert it into vapour, suffered that change at 20° or 30°, it is evident, that at 50°, 60°, or any superior temperature, it would be an air, or, in other words, permanently elastic; and if we suppose its point of vaporization to be still lower, to be 100°, or 200° below 0 of Fahrenheit, it would then be permanently elastic at any reduction of temperature we could command, and of course perfectly analogous, in its mechanical properties, to atmospheric air, or any of the gases. This inference is so evident, that we can scarcely hesitate in admitting the conclusion, that the

permanent airs are solids rarified, and rendered elastic by caloric.

The proposition is farther established by experiment. If two of these airs, which are capable of entering into chemical combination, are mixed together, they unite, and form a compound, which may exist in the fluid or solid form; and in this case the caloric, to which they owed their aëriform state, is disengaged. And chemists, by having discovered methods of producing very intense colds, have even succeeded in bringing to the fluid state some gases which formerly appeared to be permanently elastic. The objection, therefore, sometimes urged against the modern system of chemistry, that the principal substances whose actions it endeavours to trace, are hypothetical principles, is founded on very limited and superficial views.

The opinion of some chemists, that the difference between the gases and the vapours, consists in the combination of the caloric with the gravitating matter of each, being more intimate in the one than in the other, is established by no evidence. It is deduced solely from these gases being incondensible; but this is plainly owing to the cause I have pointed out, the low temperature at which these substances are disposed to pass into the aërial form.

The established chemical nomenclature is founded on these views of the nature of the aëriform state. Every air or gas is considered as a solid substance, brought into the aërial form by the agency of caloric. This solid matter cannot be obtained, because we are

unable to produce a reduction of temperature sufficient to abstract the caloric which adheres to it. But no chemist doubts of its existence. All the peculiar properties of the gas are considered as depending upon it; the form only being owing to caloric, and when it passes into chemical combinations, it is this solid matter which is considered as the agent concerned, as exerting those attractions from which the combination arises. In the usual nomenclature, then, the name of the gas is derived from this solid gravitating matter which is its base. Thus a peculiar gas has been discovered by chemists, which has the power of supporting, in a remarkable manner, combustion and animal life. It is termed Oxygen Gas; and its solid base simply Oxygen. This oxygen has never been obtained alone; but it exists, in a concrete form, in many combinations, and, when separated from these, it instantly attracts caloric, passes into the aëriform state, or forms oxygen gas. Another air has been discovered, extremely light, and highly inflammable; it is named Hydrogen Gas, and it likewise, according to those principles, is conceived of as consisting of a solid base, hydrogen, with a large quantity of caloric. The same nomenclature is extended to all the other airs.

The transition of bodies to the aëriform state is much influenced by pressure. This resists their expansion, or the repulsion established between their particles, by the agency of caloric; and hence, to convert a fluid into vapour, a higher temperature is requisite when pressure is present than when it is re-

moved. Under the usual atmospheric pressure, water boils at 212° of Fahrenheit; but it undergoes the same change at 180°, or even some degrees lower, when placed on the plate of the air-pump, and the air exhausted. At different barometrical altitudes, it boils at different temperatures; at that of 26, for example, it boils at 205°. Ether, which requires a temperature of 104°, boils rapidly in the exhausted receiver of the air-pump at the common temperature of the atmosphere; and there is every reason to believe that quicksilver passes into vapour *in vacuo;* so that even the Torricellian vacuum cannot be regarded as a perfect one. Pictet has remarked in particular, that when the barometer is exposed to considerable changes of temperature, occasionally to the solar light for example, that very small drops of quicksilver, collect in the upper part of the tube, which increasing at length by their weight, fall back into the fluid beneath *.

Pressure has an equal effect in repressing the elasticity of vapour, after the elastic state has been assumed, and by applying it in sufficient force, the vapour is entirely condensed.

It thus appears, that the change of a fluid into vapour, is not confined to a certain temperature, but takes place through an extensive range of temperature, less being formed as the temperature is low. Nor is it solely dependent on temperature, but on temperature modified by pressure; so that the pres-

* *Essais de Physique*, p. 154.

sure varying, while the temperature remains the same, or the temperature varying while the pressure is constant, variable quantities of vapour are formed. Hence it follows, that the amount of elasticity from a vapour, arising from a fluid under these different circumstances, is very different. This subject has been ably investigated by Mr Dalton; and from an extensive series of experiments, he has shewn the elastic force exerted by vapours, measured by the column of mercury they sustain, through an extensive range of temperature.

Thus the vapour of water, at the temperature of 212°, sustains a column of mercury of 30 inches; at 122°, or the mean between its usual freezing and boiling points, it is equal to that of 3.5 inches; and at 32°, to 0.2 inches. Mr Dalton having observed, that in the numbers given by his experiments, as expressing the elastic force of steam at different temperatures intermediate between 32° and 212°, there appeared to be a geometrical progression, the ratio being, however, a gradually diminishing one, was enabled, without the aid of experiment, to fill up by interpolation, those degrees which he had not ascertained by actual experiment, and to extend a table of these forces at both extremes, that is, below 32°, and above 212°; the ratios for each interval of $11\frac{1}{4}$ degrees below 32°, being 1.500, 1.515, 1.530, 1.545, &c.; and the ratios for each interval above 212°, being 1.235, 1.220, 1.205, 1.190, 1.175, 1.160, 1.145, 1.130, &c. On this principle, he constructed a table of the force of vapour from water, in every tempera-

ture from below 0 to 325°. It will be sufficient, instead of giving the full table, to give the numbers to every tenth degree *.

Temperature.	Force of Vap. in inches of Mercury.	Temperature.	Force of Vap. in inches of Mercury.
°		°	
−40	,013	150	7.42
−30	,020	160	9.46
−20	,030	170	12.13
−10	,043	180	15.15
0	,064	190	19.00
10	,090	200	23.64
20	,129	210	28.84
30	,186	220	34.99
40	,263	230	41.75
50	,375	240	49.67
60	,524	250	58.21
70	,721	260	67.73
80	1.00	270	77.85
90	1.36	280	88.75
100	1.86	290	100.12
110	2.53	300	111.81
120	3.33	310	123.53
130	4.34	320	135.00
140	5.74	325	140.70

From this table, then, we discover, what quantity of vapour is produced from water, at a certain temperature, measured by the column of quicksilver it sustains; water, for example, at a medium temperature that of 55° of Fahrenheit, giving vapour which sustains a column of 0.443 inch; and hence also, we discover at what temperature, and under what pressure, vapour will be formed. Thus, at 55° it is produced, when the pressure is that which has just been

* Manchester Memoirs, vol. v. p. 559.

stated, 0.443 inch of mercury. It is not to be conceived, as it might be perhaps from the way in which the fact is expressed, that, under these different circumstances, the same quantity of water passes into vapour, and that this vapour has more or less elasticity; but that different quantities of it pass into that state; the quantity being greater at a given temperature, as the pressure is less, or under a given pressure, as the temperature is high; and hence the exertion of a greater elastic power.

Other experiments, which have been made on the force of watery vapour, at different temperatures, particularly those by Bettancourt, which are the most extensive, and perhaps the most accurate, give numbers somewhat different; being less in the lower part of the scale, and greater in the higher. This will be apparent from the following table, in which the force of vapour, every ten degrees of Reaumur's scale, is expressed by the column of mercury, measured by inches which it sustains *.

Temperature. Reaumur.	French inches.	Fahrenheit.	English inches.
0	0.00	32	0.00
10	0.15	54.5	0.16
20	0.65	77	0.69
30	1.52	99.5	1.62
40	2.92	122	3.11
50	5.35	144.5	5.71
60	9.95	167	10.61
70	16.90	189.5	18.02
80	28.00	212	29.86
90	46.40	234.5	49.49
100	71.86	257	76.57
110	98.00	279.5	104.52

* *Journal Polytechnique*, cahier ii. p. 47.

Mr Dalton has remarked, that the assumption of the force of vapour at 32° of Fahrenheit is nothing, renders the numbers incorrect in the lower part of this scale; and that in the higher part they are represented as too great, owing, as he supposes, to a portion of air being disengaged from water by heat mixing with the steam, and augmenting its elasticity. This, admitting the observation to be just, as it probably is, may render the theoretical solution of the law of the production of vapour incorrect; but as this disengagement of air will probably always take place in actual experiment, it is not less true, that in the application to practical purposes, to calculating, for example, the force of steam, as a mechanical power, the numbers deduced in this way are to be preferred.

Mr Dalton extended his experiments to other fluids, and established, as the result of them, the general law, "That the force of vapour from all liquids is the "same, at equal distances above or below the several "temperatures at which they boil in the open air." Thus, the elastic force of the vapour of water heated to 212°, is equal to a column of mercury 30 inches in height; by a diminution of temperature equal to 30 degrees, its elasticity is diminished one half, so the vapour of any other liquid loses half its force, by a diminution of temperature equal to 30 degrees below that at which it boils under a common atmospheric pressure; and the like for any other increment or decrement of heat. When the elastic force, therefore, of the vapour of water at different temperatures is determined, it is easy to find that of any other liquid,

the boiling point of which is ascertained, the elasticity of the vapour of that liquid, at any distance from its boiling point being the same as the elasticity of the vapour of water at the same distance from *its* boiling point.

The elasticity of the vapours of different liquids, is in proportion to their volatility, as is of course to be presumed. The boiling points of ether, according to Mr Dalton, being 102°, of alkohol 175°, of liquid ammonia 140°, of liquid muriate of lime 230°, the force of the vapour of each, at 60°, is as follows: that of ether is equal to 12.13 inches of mercury; that of alkohol 1.5; that from liquid ammonia, 4.3; that of the vapour from liquid muriate of lime, about 0,26 of an inch *. Those of mercury and sulphuric acids, at low temperatures, could not be ascertained. The experiments of Bettancourt on the vapour of alkohol, give results somewhat different from Mr Dalton's; the proportion in its force to that of watery vapour being stated, at all temperatures, as more than double, or as 7 to 3 nearly †.

By increasing pressure on fluids, they may be heated to a very high temperature. In Papin's digester, a close iron vessel, in which, by means of a valve on which a regulated weight presses, vapour may be retained without the risk of bursting the vessel, until it exert a very great pressure. Water has been heated to above 400°, and, by this increase of temperature,

* Manchester Memoirs, vol. v. p. 563, &c.

† *Journal Polytechnique*, cahier ii. p. 48, 49.

its solvent power with respect to many substances is much increased.

Bodies passing into the aëriform state, absorb a very large quantity of caloric, which does not increase their temperature, and give it out again when reduced to the fluid state. The consideration of this important phenomenon will be introduced with more advantage, in connection with another subject; the quantities of caloric which bodies contain.

From the different tendencies which bodies have to pass into the state of vapour, we are enabled to separate them from each other when they are previously combined, or when they become products of chemical action; and peculiar arrangements, adapted to different cases, being requisite for this purpose, constitute several chemical operations relative to vaporization, which, with the apparatus in which they are performed, it is necessary to describe.

When heat is applied to recover a solid substance dissolved in a fluid, without any arrangement being made to preserve the fluid itself, the operation, which is named Evaporation, is performed in shallow vessels, which, presenting an extensive surface, proportioned to the depth of liquor, admit of it being quickly heated, and of the vapour escaping without any resistance. These vessels are of glass, earthen-ware, or metal, according to the nature of the substances operated on, and the degree of heat which is to be applied. In chemical experiments on a small scale, basons of glass, or of Wedgwood's earthen-ware, sometimes

also of silver or platina, are used, the heat being applied by the medium of a sand-bath. In pharmacy and the arts, they are more frequently constructed of iron or lead, and the heat is directly applied. Count Rumford has endeavoured to determine the capacity of boilers, best adapted to the evaporation of water, from a given quantity of fuel; and the same subject has been made the subject of experiment by Hassenfratz, who has added some experiments on the comparative results of evaporation at different temperatures. The result with regard to the last, is, that it is most economical to keep the liquor up to its boiling point, the greatest quantity being thus evaporated with the least consumption of fuel *. At the same time, it frequently requires to be attended to, not to raise the heat unnecessarily high, as the vapour, by its affinity to the fixed body, elevates part of it with it in a combined state. This has been ascertained even with regard to the most fixed salts, when water is evaporated from them at a high heat.

When the object is to obtain the volatile matter by evaporation, it is of course carried on in close vessels, constructed so as to collect and condense the vapour. The operation is then named Distillation. Different kinds of distilling apparatus are employed, adapted to different purposes.

Where the process is conducted on a large scale, as in the distillation of ardent spirits, the common still,

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* *Journal Polytechnique*, cahier vi. p. 364.

made generally of copper, is employed. The construction of this has always been very faulty, and in direct opposition to the principles which ought to have been followed. Being made of a very considerable depth, proportioned to its diameter, a large body of liquor is required to be heated, while comparatively a small surface was exposed to the fire, and hence a waste of heat. And the tube issuing from the head of the still, and conveying the vapour into the spiral tube placed in the refrigeratory, being generally very narrow, the vapour was in some measure accumulated, and by its pressure on the liquor retarded the evaporation. In this country the construction of the common still, has, within these few years, received very great improvements, by the skilful application of the principles which regulate distillation.

In the greater number of chemical operations, metallic vessels are acted on either by the materials, or by the product of the operation; and hence glass vessels generally require to be employed in distillation. The retort or conical bottle, the neck of which is bent at an angle of about 60 degrees, A adapted to a receiver B, (Fig. 35, Plate V.) is the most convenient apparatus of this kind. Sometimes it is convenient to have it tubulated, as in Fig. 36, A, and to have the distance between it and the receiver increased, so that the latter may be kept sufficiently cool, by an intermediate tube B or adopter as it is named. The heat is applied to it by the medium of a water-bath or sand-bath. Sometimes it is made of earthen-ware, where it is designed to be exposed to a very intense

heat, and is covered with a coating of clay and sand when the fire is to be immediately applied to it.

In some cases of distillation, the product is not entirely a mere vapour, which may be condensed, but there is likewise disengaged a permanent gas, which is incondensible, but which still may require to be collected. The receiver having a bent tube issuing from it, represented by C, Fig. 36, is employed in this case, the condensible part of the product is collected in the body of the receiver, and the elastic product issuing through the tube, which is placed in a vessel of water, may be collected in an inverted bottle or jar.

In certain cases, the product designed to be obtained by distillation, is an elastic fluid, not condensible by itself, but capable of being condensed by being transmitted through water, with which it is retained in combination. The apparatus invented by Woolfe, Fig. 37, is employed for this purpose. It consists of a series of bottles, A, B, C, D, connected with each other by bent tubes, and connected with a retort generally by the medium of an adopter. The first bottle A is designed to collect any condensible part of the product. In the other bottles, water is placed to nearly one half their height, represented in the figure by the dotted line, and the tube passing from the one into the other, beyond the second bottle B, dips into the water of the bottle into which it is inserted, as is represented in the plate. The gaseous product is thus transmitted through the water, by which, as well as by the pressure which is necessarily exerted by the

short column of water in each tube, its absorption is promoted; and if any portion is incapable of being absorbed by the water, it passes off by the bent tube at the end, and may be collected in an inverted jar, in a trough of water. Each of the bottles except the first, has a straight tube, which rises to the height of 8, 10 or 12 inches above its insertion into the bottle, and passes so far within it as to dip in the water nearly half an inch. This tube is termed the tube of safety, and the use of it is to guard against that reflux of fluid which might happen from a partial vacuum arising from condensation in any of the bottles. At the commencement of the distillation, the joinings of the tubes with the bottles being well secured, the whole is air-tight; and, by the gas produced, the atmospheric air contained in the upper part of the bottles is in a great measure expelled through the tubes. If, therefore, in any stage of the distillation, the production of gas should diminish, the quantity contained in the bottles being absorbed by the liquor, a partial vacuum is formed, and at the end of the process, when the retort cools, this must always happen; the consequence of this must be, that the water being more pressed on by the atmospheric air without, than by the gas within, must pass backwards from one bottle to another, by rising through the tubes, as from D to C and from C to B, and thus the whole will be mingled together, which would often defeat the object of the distillation. This, however, is effectually prevented by the tubes of safety, as, when any such partial vacuum happens, the atmospheric air

is forced through the small quantity of fluid in which they are immersed, and rising into the bottles, preserves the equilibrium.

Various improvements have been made in this apparatus. One defect in it is, that we cannot have the advantage of the immersion of the tube which comes from the first bottle A into the liquid in the second B; for as the first bottle, or globe as it sometimes is, is designed to collect the condensible product, and ought therefore to be without water, it can have no tube of safety; and hence, if the tube issuing from it dip into the liquid in the second, whenever any condensation happens, from the gas ceasing to be produced, the liquor will pass backwards into it. The apparatus, therefore, is represented in the plate, as it ought to be, with the bent tube from the first bottle only reaching near the surface of the liquid in the second, while in all the others it is immersed. As the liquid, however, in the second bottle, is in the best situation for being impregnated with the gas, and therefore for forming the most concentrated product, it is of some importance to aid this as much as possible, and obtain the advantage of the gas being forced to pass through it, by the tube passing into it being immersed. The contrivance that has been used for this purpose, is the tube of safety of Welther, or bent tube with an additional curvature, and a spherical ball, represented Fig. 38 as intermediate between the globular receiver and the common Woolfe's bottle, and connecting them. In this is put a small quantity of water, so as to rise, when the pressure without and within is equal, about

half way into the ball. If the elasticity is increased in the internal part of the apparatus, during the distillation by the production of gas, the water is pressed upwards to the funnel at the top; if there is a condensation, it is forced by the atmospheric pressure into the ball, but whenever it has passed the curvature beneath the ball, it is obvious that a portion of air must rise through it, and will pass into the globe or bottle, to the tube of which this bent tube is adapted. This tube, however, though it may answer the purpose, is inconvenient; from its form, it is very liable to be broken; and, what is its principal defect, we can employ no great pressure in the apparatus with it, without making it of such a length as to be unwieldy and subject to risk. The method I employ to obviate this inconvenience is more simple. It is having the usual bent tube constructed with a ball in that part of it which is inserted in the bottle containing the liquid into which it is to dip, as represented Fig. 39. By properly proportioning the depth to which the tube is immersed in the liquid in B, to the size of the ball, it is obvious, that when from any condensation in A the liquor in B rises, when the ball is filled, the extremity of the tube will be no longer immersed; a portion of the gas present will therefore rise in it through the water, and preserve the equilibrium, so that if the tube be not too deeply immersed, no part of the liquid in B can ever pass into A. This method has the advantages that we can employ any pressure whatever in the apparatus, and that no atmospheric air is introduced in the course of the distillation

into the first bottle, but only the elastic fluid which is the product of the process. The use of tubes of this kind may even supersede the use of tubes of safety through the whole apparatus; for, if each have a spherical cavity in its long leg above its insertion in the bottle, and if its immersion in the liquid be duly proportioned, the reflux of the liquid will be prevented, in the manner just now explained, while any extent of pressure may be obtained by a tube issuing from the last bottle being immersed in water or quicksilver.

Another imperfection which attends the common Woolfe's apparatus, is the difficulty of adapting the tubes by grinding, so that it is necessary to secure the joinings by lute, which is always inconvenient. I have sought to remedy this, by having a tube fixed or soldered when the bottle is made, into that orifice into which the long leg of the tube from the preceding bottle is to enter, as represented Fig. 40, in the bottles B, C, D. This soldered tube being of such a length that it is immersed in the liquor within the bottle, and the tube which enters it having a very slight curvature at its extremity, which throws the gas beyond the extremity, it cannot return, but must pass forward into the next bottle; and as there is no difficulty in grinding the tubes into the bottles *from* which they issue, the whole apparatus is easily constructed without the necessity of lute. The open tube, too, serves the purpose of a tube of safety. The deficiency of an apparatus of this construction, is, that very little pressure can be applied to promote the absorption of the gaseous product by the liquor, as, from

the shortness of the open tubes, the liquor, by such a pressure, is forced up them, and may overflow, though this may to a certain extent be obviated, by having the wide open tubes not soldered, but ground in, and having them of such a length as will admit of the rise of the liquid, as is represented in E. The only difficulty in executing this, is to have the orifice of the bottle into which the wide tube is ground perfectly straight, and the smaller tube which enters it precisely at a right angle, as otherwise it cannot be inserted, at least without having the wide tube of too great a diameter. With care, however, this may be attained, and the apparatus then answers perfectly well. A is as usual left without water, and therefore cannot have an open tube, but absorption is guarded against, either by the tube passing from it not dipping in the liquor in B, or by having a ball, as is represented in the figure. Other improvements of the original apparatus have been proposed,—one by Mr Burkitt *, in which a valve is introduced; one of a similar kind by Mr Pepys, and another by Mr Knight †.

What, upon the whole, however, will be found the most convenient apparatus of this kind, is one described by Dr Hamilton, in his translation of Berthollet's Treatise on Dyeing, represented with some slight variations, Fig. 41. It consists of a series of

* Nicholson's Journal, 4to, vol. v.

† Philosophical Magazine, vol. xx.

globes, which are ground into each other. The first is inserted into the second by a short neck, for the reason already stated under the description of the former apparatus, that, being designed to receive the condensible product, water cannot be put into it at the commencement of the distillation, and therefore a tube of safety cannot be inserted; and hence the tube by which it is connected with the second bottle, cannot dip into the water in that bottle. From the second, however, there passes a tube, having such a curvature that it can be easily introduced into the third, and be immersed in the water which it contains; the third has a similar curved tube, which passes into the fourth, and the fourth terminates by a bent tube in a small pneumatic trough *. In the second bottle is inserted a tube of safety. In the other bottles this is not necessary, as the condensation in them is never considerable. The great advantages of the apparatus are, that all the parts of it can be very easily adapted by grinding, and that it is not liable to be broken by any slight dislocation, as the tubes merely recede from the bottles in which they are inserted; advantages which cannot be obtained when the tubes are bent as they are in the common apparatus. The only deficiency is, that as the tubes cannot have such a cur-

* In the original apparatus, these curved tubes are adapted to the necks of the globes, from which they issue by grinding, but this is unnecessary, as the globes can be easily made with such curved tubes projecting from them.

vature as to be made to dip more than an inch in the water, and scarcely so much without employing too much water, the degree of pressure cannot be great, so as to facilitate the absorption of the gas. I have obviated this, by connecting with the last bottle, in the cases where it is required, a tube bent at right angles, like the common bent tube of the Woolfe's apparatus, which is immersed in a jar of water to the depth that may be required; and by substituting quicksilver for water, any pressure that the apparatus can sustain, may be obtained.

When the product of volatilization is a substance which condenses in the solid form, the process is named Sublimation; and as such products are in general easily condensed, a simple apparatus only is required. The alembic with its capital, Fig. 42. Pl. VI. is that generally used. The alembic A is merely a conical shaped vessel of glass, in which the materials are put, and exposed to heat in a sand bath, the sublimate condensing in the upper part of it, and forming a crust on its sides. The capital B is adapted to its mouth to prevent the escape of the vapour; a small groove or channel runs in the under part, terminating in a tube projecting from it, by which any liquid is collected and prevented from running down or dropping on the sides of the alembic.

I have, lastly, to take notice of the apparatus requisite for operating on bodies which are permanently elastic.

The pneumatic trough is the principal part of this apparatus. It is merely a trough, made of wood, lined with lead, generally of an oval form, about 6 inches

deep, from 20 to 24 in length, and at the greatest breadth 15 inches; a moveable shelf being placed in it, at the depth of $1\frac{1}{2}$ or 2 inches from the edge, in the longest direction, so as to occupy one-half of the breadth, as is represented in Fig. 47. If a glass jar be filled with water, and placed inverted on this shelf, the trough being filled with water to the edge, it is obvious that the mouth of the inverted jar being surrounded with water, the water within it will be sustained by the pressure of the atmosphere. If while thus filled, the extremity of a retort, or tube connected with a bottle disengaging gas, be placed under it, or if another inverted jar, containing any air, be turned up, under the mouth of it advanced of course a little over the shelf, the elastic fluid, in either case, will rise through the water, displace it, and be collected in the jar; and while the mouth of this jar continues surrounded with water, the included air cannot escape, nor will the atmospheric air find access to it. In this way, then, aëriform fluids can be collected, preserved, and easily submitted to experiment. Some of them, however, are rapidly absorbed by water. These must be received and kept over quicksilver; and as this fluid is both expensive, and inconvenient from its weight, a smaller trough is employed, either hollowed out of marble, or of a solid block of hard wood. This is represented, Fig. 48. with an addition which is convenient;—a small rod fixed in the wooden standard on which the trough is placed, which, by a ring attached to it by a sliding arm, serves to support, without any

risk, the jar filled with quicksilver, and placed on the shelf.

The other principal part of the apparatus, for operating on the gases, is the Gazometer, designed to contain gases so that measured quantities can be withdrawn, of which there are some more, others less complicated. One of the most simple, and which answers sufficiently, at least for all common experiments, is that represented Fig. 49. It is made of tinned iron, the surfaces of which are japanned, and consists of two principal parts; a large vessel A, somewhat bell shaped, which is designed to contain the gas, and a cylindrical vessel of rather greater depth, B, in which the former is placed, and which is designed to contain the water by which the gas is confined. To diminish, however, the quantity of water, this cylindrical vessel has a cone within it, also of japanned tinned iron, C, adapted to the shape of the gas-holder, so that this latter slides between this and the cylindrical vessel, and a small quantity of water is sufficient to fill up the space between them. The vessel designed to contain the gas, is suspended by cords hung over pulleys, to which weights are attached, so as to counterpoise it. From a stop-cock at the under part of the apparatus, D, there runs a tube under the cylinder, which rises through the centre, passing through the cone, the opening by which it passes being soldered so as to be air-tight, and terminating by an open mouth at the upper part of the bell shaped vessel A. This tube, at the part where it is bent at right angles, to ascend as has been described, is connected with another which also runs under the

bottom, and ascends on the outside, terminating in the stop-cock E, so that from the one stop-cock to the other, through the gas-holder, there is an uninterupted passage. When the instrument is to be used, the stop-cock E is opened, and the vessel A pressed down, a sufficient quantity of water being in the outer cylinder; the air of the vessel is forced out by the pressure, and its place is occupied by the water in which it is thus immersed. When this is effected, the stop-cock is closed, and now, if we wish to introduce any gas into the apparatus, a bent funnel, the mouth of which is placed in a vessel of water, is attached to the tube of the stop-cock D, as represented in the figure, and the stop-cock is opened. If the extremity of a retort, or of a tube conveying gas, as represented in the figure, terminate below the orifice of the funnel, the gas will rise along the tube, will ascend to the top of the gas-holder, and this being counterpoised, will, as the gas enters, rise in the water until it is filled, a quantity of water, of course, remaining around the mouth of it, by which the gas is confined. When we now wish to expel the gas, the stop-cock D is closed, that at E is opened, a flexible tube is adapted to it, and the gas-holder being pressed down, either by the hand, or by its own weight from the removal of the counterpoising weights, a stream of gas issues from the extremity of the flexible tube, and may be transferred into a jar, or be applied to any other purpose, and its quantity may be measured by the instrument being graduated by a scale marked on the rod F.

The instrument which appears connected with the gazometer in the plate, Fig. 50. is a very convenient one for procuring gases from any solid materials, by the application of a strong heat. It is an iron bottle A, into which is fitted, by grinding, a tube bent at an acute angle. To this a smaller tube is adapted, the extremity of which can be adapted to various heights, by a circular joint in the middle of it, at *b*. The bottle containing the materials from which the elastic fluid is to be disengaged, is placed in a furnace, or in a common fire, so as to be raised to a sufficient heat, the gas issues at the extremity, and may be conveyed into the gazometer, or received in an inverted jar on the shelf of the pneumatic trough. At the end of the operation, the gas ceasing to be produced, as the heat diminished, the water would be pressed into the tube, and might rise even into the bottle, if the joinings were not opened. The easiest way of obviating this, is by having a small stop-cock in the tube as at *c*, which may be opened when the production of the gas has ceased.

When a gas is extricated, in consequence of chemical action, with the application only of a moderate heat, the flask or cucurbit, with a bent tube ground to it, Fig. 43. is the most convenient.

In all accurate experiments on gases, it is of importance that the quantities should be measured with precision; and as to weigh the gases requires a very delicate and complicated apparatus, and is troublesome in the execution, chemists measure them by their volumes, and find their weights by a reference to the tables of their specific gravities, which have been constructed.

Hence jars graduated into cubic inches and tenths, are convenient, as are also in other cases, jars graduated into equal arbitrary parts, as represented Fig. 44. In thus estimating the weights of gases from their volumes, several circumstances require to be attended to, particularly the temperature and the pressure. Elastic fluids being so expansible, it is obvious that a very considerable change in their specific gravity will be made, by a very trivial alteration of temperature. The standard temperature of 54.5 of Fahrenheit is assumed as that at which the specific gravities of the gases are ascertained, and if their temperatures are different from this, the due correction is to be made. The formula given by Lavoisier, on the assumption that the gases are expanded $\frac{1}{472}.5$ for each degree of Fahrenheit, is simple. Divide the observed volume of air by 472.5, and multiply the quotient by the degree of temperature above or below 54.5, the correction being negative when the actual temperature is above the standard, and positive when below. If the gases expand $\frac{1}{480}$ for each degree of Fahrenheit, as we have some reason to believe they do, this of course ought to be the number taken as the divisor.

The other correction that may be requisite is, *that* for any varying pressure, whether of the atmosphere, or of any fluid in which the vessel containing the gas may be more or less immersed. The weight of the gases is fixed at the mean barometrical pressure 29.85 inches of mercury; and of course, if the atmospheric pressure, at the time of estimating the volume of a gas, vary from this, the correction must be made to

bring it to the standard. Another correction which may be requisite is, *that*, from the pressure of the fluid surrounding the mouth of a jar containing air. If a jar containing air, stand on the shelf of the pneumatic trough, and if the water, without and within the jar, be precisely at the same level, it is obvious that the pressure is equal, and is merely that of the external atmosphere; but if it be surrounded without with water, to a greater height than that within, to that, for example, of two inches, it is equally evident, that there is this additional pressure to that of the atmosphere on the included air; and if it were surrounded with quicksilver, as the weight of this is so much greater, the pressure must of course be proportionally more considerable; or if the jar were only $\frac{3}{4}$ths filled with air, the other fourth being filled with water or quicksilver; it is also obvious, that this counteracts the pressure of the atmosphere on the gas included, and that the real pressure to which it is subjected, is the atmospherical pressure *minus* the weight of the column, whether water or quicksilver, within the jar, which of course must be allowed for. Ample details on every thing relating to this subject, connected with pressure and temperature, will be found in the third part of Lavoisier's Elements of Chemistry, and tables are given by Mr Kirwan, in his Treatise on Mineral Waters, of the correspondence between the real and the observed volumes, where the pressure is varied by different heights of water or mercury. The method always to be prefer-

red, where it is practicable, is to bring the fluid without and within the vessel to the same height.

IGNITION.

The effects arising from the operation of Caloric, which we have hitherto considered,—Expansion, Fluidity and Vaporization, are so far connected, that they may be regarded as different degrees of one more general effect,—the increase which it occasions in the distances of the particles of bodes. Ignition, or Incandescence, cannot be referred to this cause, and is therefore an effect of caloric, having no immediate connection with the others.

By Ignition, is meant that illumination or emission of light, produced in bodies by exposing them to a high temperature, and which is not accompanied by any other chemical change in them. It is to be distinguished from combustion, a process in which there is also the emission of light and heat. Combustion is always the result, not of mere increase of temperature in the body which suffers it, but of the chemical action of the air, or of a principle which the air contains. A certain class of substances, therefore, denominated Combustible, are alone susceptible of it, and when the process has ceased, the body remains no longer combustible. Ignition is an effect of the operation of caloric alone; it is wholly independent of the air, for by immersing completely any body in melted glass, it is rendered luminous; all bodies, at least all solid and liquid substances, are equally susceptible of it; and if it has ceased from a reduction

of temperature, it may be renewed by the temperature being again raised.

The point of temperature at which the first stage of ignition takes place, or at which, in common language, bodies arrive at a red heat, appears to be the same in all. Mr Wedgwood gilded lines running across a piece of earthen ware, and luted it to the end of a tube, which was placed in a heated crucible; the eye being applied to the other extremity of the tube, no difference of time could be perceived in either the gold or the earthen-ware beginning to shine. No two substances can be more dissimilar; and it may be inferred, that all bodies become red-hot at the same temperature. As this can be judged of only by the illumination, it must of course appear various, according to circumstances. In a body, therefore, which in the dark appears at a low red heat, the illumination will not be visible in day-light. Sir Isaac Newton, by observing the celerity with which a body cools, and calculating on the principle which has been already pointed out (p. 161.), concluded, that ignition, visible in the dark, corresponds with 635° of Fahrenheit's scale; full red heat with 752°; and ignition visible in day-light with above 1000°. Dr Irvine, having found that quicksilver boils at 672°, and having observed that boiling mercury did not appear at all luminous in the dark, it necessarily followed, that the point of ignition must be higher than Newton had supposed it to be. He had farther found, that when equal *bulks* of iron and water, at different temperatures, are mixed together, the resulting temperature

is nearly the *mean*, and he applied this method to determine the point of ignition: the result is not precisely known; but the heat of a common coal-fire he found to be 790° or 796° *. Mr Wedgwood, by the expansion of the piece of silver, measured by a gage of baked clay, by which he endeavoured to connect his thermometer with Fahrenheit's, as has been already explained, fixed the point of ignition visible in the dark at —1 of his scale, which corresponds with 947° of Fahrenheit; and ignition, in day-light, he placed at the commencement of his scale, or 1077°. This differs from the preceding results; and as it is probable that the silver would suffer an increasing expansion, this might cause the temperature to appear higher than it actually was, and hence have given the point of ignition too high. It is probably not far from 800° of Fahrenheit.

By raising the temperature, the illumination becomes brighter, and the red light acquires a mixture of yellow rays. At length, by increasing the heat, we have the due proportion of coloured rays, which forms perfectly white light. This is the highest state of ignition, or any farther rise of temperature produces no apparent change.

Ignition continues undiminished, as long as the temperature is kept up, unless the heat be such as to volatilize or alter the constitution of the ignited body.

The aëriform fluids are not brought into a state of

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* Chemical Essays, p. 33.

illumination by heat. This was observed by Dr Fordyce, in the example of the vapour, at the end of the flame of a blow-pipe, which though itself not visibly luminous at its extremity, will, if applied to glass, raise it to a white heat *. The fact was afterwards also established by Mr Wedgwood. Air was forced to pass through an earthen tube, in a state of ignition, and was conducted into a globular vessel, from which, by an opening in the top, it was allowed to escape; while, by another opening in the side, closed by a piece of glass, the eye could be directed into the inside of the globe. On looking into it, the air which had passed through the ignited tube was not luminous; but if a solid body, as a piece of gold, was suspended in it, this became luminous †. This is probably owing to the tenuity of aëriform fluids, whence they present too few points in a given space to project a quantity of light sufficient to excite vision.

The phenomena of ignition are produced not only by the application of heat, but likewise by friction and attrition. When a piece of steel is struck against a flint, small particles of the metal are detached, which are at a red heat. Or if various hard minerals be made to act strongly against each other, they give out light. By applying, for example, quartz or agate to the circumference of a wheel of fine grit, revolving at a moderate rate, Mr Wedgwood observed, that the substance applied became brightly red even in day-

* Philosoph. Trans. vol. lxvi. p. 504.

† Ibid. 1792.

light, at the touching part; if the wheel revolved at a quicker rate, the part in contact emitted a pure white light; and in both cases, glowing sparks were continually emitted, some of which were not extinguished before they had passed twelve or fourteen inches through the air. They exploded gunpowder and inflammable air, and burnt the skin, a sufficient proof that they were not merely luminous or phosphorescent, but ignited, or at a red heat. In the same mode, glass and porcelain were raised to a red heat. These appearances from attrition, are probably to be ascribed to the heat which is excited, rising sufficiently high to extricate their light, as the same bodies become luminous when directly heated, and as the same appearances are not produced in substances which are soft, these not having their temperature raised by attrition *.

On the cause of ignition different opinions are entertained, and the question is not yet determined. Those who suppose light and caloric to be modifications of the same substance, and to be mutually convertible, regard the phenomena of ignition as arising from the conversion of caloric into light,—an hypothesis, as I shall afterwards have to shew, extremely improbable. Others have supposed, that the light extricated is a constituent principle of the ignited body, and is expelled by the repulsive agency of ca-

* Philosoph. Trans. for 1792, p. 39.

loric. The objection to this opinion is, that, admitting light to exist in incombustible bodies, as indeed we know from the phenomena of phosphorescence that it does, yet it must be contained in them in limited quantity, and therefore its emission in ignition should gradually diminish, and at length cease. Perhaps it is necessary to separate the causes by which ignition is effected, in the consideration of its theory. When it is excited by communication with a hot body, it probably receives from that body the light as well as the caloric. If placed, for example, amid burning fuel, both light and caloric are evolved from the combustion; the ignited body is penetrated with caloric, which it is also giving out, and that too under the form of rays, or radiant caloric; it is equally exposed to the light from the combustion; we may suppose it at that high temperature to be penetrated with it also, and to throw it off from its surface. Even when removed from the fuel, it will continue to emit both, though the supply being cut off, the emission of light ceases in a very short time, and that of caloric gradually diminishes. The experiment of Wedgwood, in which ignition was excited by applying to the body a stream of air highly heated, but not luminous, may be supposed adverse to this explanation; but I shall afterwards, in the consideration of the question, with regard to the identity of light and caloric, have to prove that it is easily reconciled with it, as the heated air, though not luminous from the cause which has been already stated, may still have conveyed light. With regard to the production of ignition by attri-

tion, the same difficulty will be found in accounting for the evolution of caloric as for the evolution of light. It is not proved that ignition can in this case be kept up for an indefinite time, as it can by communication with matter in a state of combustion; and the light which does appear may perhaps be the light contained in the body, expelled by the high temperature which the friction or percussion excites.

The effects of caloric in causing chemical combinations and decompositions have been already explained under the doctrines of Chemical Attraction, and they cannot indeed be considered as a primary effect of its operation but as resulting from the expansion it occasions; which, by weakening the attraction of cohesion in some cases, favours combination; and in others, by increasing elasticity, counteracts it, and acting unequally on the elements of a compound, separates them from each other, or gives rise to its decomposition.

Sect. III. *Of the Communication and Distribution of Caloric.*

When bodies at different temperatures are placed in contact, either directly, or by the medium of some other substance, those which are at a higher temperature part with caloric to these which are at a lower; and this reciprocal emission and absorption continue until a common temperature is formed. This fact is

extremely familiar. If a body be highly heated, it is impossible to preserve it in that state; however we may place it, it will immediately, when removed from the source of caloric, begin to give out the heat it had received, and it will continue to do so until it is at the same temperature with the bodies around it: or if we have a body which has been rendered intensely cold, it is equally impossible for us to preserve it so; it will imbibe caloric from the surrounding matter, until it has attained an equality of temperature. These changes may happen among different bodies, and under different circumstances, with different degrees of celerity, but they always take place, and to any extent.

This tendency of caloric to an equilibrium of temperature seems in a great measure to arise from its repulsive power. When a hot body is placed among others that are colder, the excess of caloric in the former leaves it, not so much from any attraction exerted to it by the other bodies, as from the tendency of caloric to exist everywhere in what has been termed an equality of tension or repulsion. The proof of this is, that a body at a high temperature, placed in the Torricellian vacuum, will have its temperature gradually reduced, the caloric emanating until it arrive at an equilibrium with that in the surrounding bodies. Yet the distribution of caloric cannot be ascribed entirely to this cause. It is not to be considered as an highly elastic fluid, retained in bodies only by the resistance opposed to its escape, from the equality of tension in which it exists at the same time

in the surrounding matter; for were it so, it ought to escape from, or enter different bodies, if they were at the same temperature, and exposed to the same medium, with equal celerity. We find this, however, not the case; and the influence of the contiguous matter on the change of temperature is even considerable. A body will be either heated or cooled faster when in contact with any material medium than when *in vacuo*, and will suffer these changes with very different celerities when in contact with different kinds of matter. A thermometer at a high temperature will be cooled more quickly if plunged in water than if suspended in atmospheric air, and still more so if plunged in quicksilver than in water. And, on the other hand, if at a low temperature, it will be heated much faster in the quicksilver than in the water, and in the water than in the atmospheric air, though the temperatures of all these may have been previously the same.

From an attentive examination of these phenomena, it has been discovered, that this propagation of caloric over matter takes place in two modes. Of the caloric emanated from a body at a high temperature, part is projected from its surface in right lines with great velocity; and another portion is communicated more slowly to the matter which is directly in contact with it, is conducted through that matter from one particle to another, and is given in like manner from it to other bodies, with a celerity greater or less, but always comparatively moderate. The former is little if at all dependent on the nature of the surrounding medium, at least if it be an elastic one, while the latter

is materially influenced by it. The distribution of caloric may be considered under these two modes—of Radiation and of Slow Communication.

SLOW COMMUNICATION OF CALORIC.

Bodies in contact with each other attain a common temperature, by the hotter communicating the necessary proportion of the excess of its caloric to the colder. The celerity of this communication is different in different bodies, some being quickly heated, and as quickly cooled; others undergoing these changes much more slowly. If a number of bodies be exposed to a common source of caloric, they will receive it, and will all at length arrive at a common temperature; but some will do so much more quickly than others; and if, after they have attained this common temperature, they be removed from the source whence they received caloric, the same difference will be observable in the celerity with which their temperatures fall. Each body always receives and parts with caloric with the same celerity; and therefore, those which are most quickly heated will be also most quickly cooled.

This permeability of bodies to caloric, or the property by which they receive and part with it when in communication with others at a different temperature, is termed their Conducting Power. Those which receive and part with caloric quickly, in other words, which have their temperature quickly altered by communication with hot or cold bodies, are said to be better conductors of caloric than those which receive and part with it more slowly.

The difference in conducting power in different bodies is extremely obvious. If a rod of iron and a rod of glass be held in the hand, the extremity of each being put into a common fire, the caloric will be propagated so quickly through the iron rod, that the hand will soon be unable to retain it; while the glass rod may be held for any length of time. Or an earthen vessel, containing water, nearly boiling hot, may be easily held in the hand for a considerable time, while a metallic vessel, containing water at the same temperature, can scarcely be touched. The same difference is conspicuous in other bodies; and scarcely two agree in the facility with which they permit caloric to penetrate their substance.

It may, in general, be remarked, that dense bodies are the best conductors of caloric; and that those which are more rare and spongy, conduct it very imperfectly. The metals which are the substances of greatest density, are those which transmit it most rapidly; earthy substances conduct it more slowly; wood is a very imperfect conductor, and the spongy materials which form the covering of animals, hair, fur, feathers, &c. are inferior to every other solid matter in their conducting power. Even the same kind of matter, in its different states of aggregation, differs in this property. An iron bar, or an iron plate, Count Rumford remarks, is a much better conductor than iron filings, and sawdust is a worse conductor than wood.

Richman made some experiments on the conducting power of various metals, with the view of discovering whether any relation could be traced between it and

some of the other properties of bodies, with which it had been supposed to be connected. His experiments were performed by taking hollow balls of the metals, which received and inclosed the ball of a mercurial thermometer. The balls were plunged into boiling water, untill the thermometer in each rose to the same point. They were then removed, and exposed to the atmosphere, and the time which elapsed while the inclosed thermometer cooled, a certain number of degrees was marked. The balls being equal to each other, the relative conducting power was thus ascertained by the times of cooling. Among the metals subjected to examination, brass and copper appeared to have the greatest power of retaining caloric, and were equal to each other; next to these was iron; then tin; and lead appeared, to use Richman's phrase, to have the least power of retaining heat, the decrements of temperature in all of them being in the following proportions: brass 10; copper 10; iron 11; tin 17; lead 25.

With regard to the general object of his experiments, Richman inferred, that the decrements and increments of temperature in these bodies, were not in the inverse ratio of their density, of their cohesion, or of their hardness, or in any compound ratio of these *, and, of course, could be discovered only by experiment.

Ingenhouz, by a different mode of experiment, en-

* *Comment. Petropol.* t. iv. p. 241.

deavoured to determine the relative conducting powers of a number of the metals. Selecting rods, or rather fine wires, of the same diameter, they were plunged into the same quantity of melted wax, to the depth of eight inches; in withdrawing them, each was thus covered with a coating of wax. When cold, they were plunged into heated oil, to the depth of about two inches. On withdrawing them, the length of wax coating melted shewed the extent to which the heat had penetrated the metal, and, by this, their relative conducting powers. Silver he found to be the best conductor, gold held the second place, tin and copper were next, being nearly equal; next to these were platina, steel, iron, and lead, which did not differ much; lead, however, was evidently the worst conductor *.

We perceive from this table, that although density is favourable to the transmission of caloric through bodies, yet the conducting power is not precisely as the density; copper and tin, which are much lighter than platina and lead, being better conductors. The experiments of Ingenhouz, though they cannot be regarded as perfectly accurate, are superior to Richman's, as, in the latter, the discharge of caloric by radiation is not separated from that by communication.

No accurate experiments have been made on mineral substances as to their conducting powers. Meyer has made some experiments on the conducting powers of different woods. He formed solid balls of them, of

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* *Journal de Physique*, t. xxxiv. p. 68.

equal diameter, and made a cylindrical cavity in one side, which penetrated to the centre, and in which the bulb of a thermometer was introduced, the cavity being filled up with dust of the wood of which the ball was framed. Prepared in this way, they were successively heated, until the thermometer in the centre indicated a certain temperature; the ball was then suspended in an atmosphere, the temperature of which, of course, in the different experiments, was the same; the time requisite for its descent a certain number of degrees, was marked, and thus the conducting powers could be compared. The following table exhibits the results:

Elm, -	1000	Spruce-fir, -	1196
Pedunculated oak,	1003	Birch, -	1047
Apple-tree,	841	Alder, -	1182
Pitch-pine -	1152	Scotch-fir, -	1189
Pear-tree, -	1022	Sessile-leaved oak,	1117
Ebony, -	667	Beech, -	987
Ash, - -	946	Lime-tree, -	1198
Horn-beam, -	992	Plum-tree, -	998

In such experiments, however, there are some sources of fallacy, which render the results doubtful. The communication or abstraction of caloric by radiation, as has been observed, has not been sufficiently distinguished from that by slow communication; and due attention has not always been paid to the quantities of caloric requisite to produce changes of temperature in different bodies. This last circumstance has been remarked by Humboldt, who has given a table of the

conducting powers of a number of bodies, in the *Journal de Physique*, t. xliii. p. 306. It appears, however, to be so inaccurate, and to contain such discordant results, that no confiden an be placed in it.

Count Rumford, with the view of discovering the relative degrees of warmth of the different articles of clothing, made experiments on the substances of which they are composed. The method he followed was, to suspend a thermometer in a cylindrical glass tube, the extremity of which had been blown to a globe, $1\frac{6}{10}$ inch in diameter, the bulb of the thermometer being in the centre of the globe. It was then surrounded with the substance, the conducting power of which was to be determined. The instrument thus prepared was heated in boiling water, and afterwards being plunged into a freezing mixture of pounded ice and water, the times of cooling were observed, and noted down *.

Having ascertained the time that was requisite for the thermometer cooling, a certain extent of the thermometrical scale, when surrounded with air, he repeated the experiment with the following substances, raw silk, wool, cotton, linen in the form of the finest lint, the finest part of the fur of the beaver, the finest part of the fur of a white Russian hare, and eider down; 16 grains of each of these being successively introduced into the globe of the instrument. The following are the results; the number of seconds being marked, during which the thermometer

* Essays by Count Rumford, vol. ii. p. 428.

cooled 60 degrees, or from 70° to 10°, of the scale of Reaumur. Air, 576″; raw silk, 1284″; wool, 1118″; cotton, 1046″; fine lint, 1032″; beaver's fur, 1296″; hare's fur, 1315″; eider down, 1305″. The relative conducting powers are thus shewn, being inversely as the times of cooling; hare's fur and eider down are the worst conductors, lint the best. The same experiment was repeated with fine powder of charcoal, lamp-black, and pure dry wood-ashes. The total times of cooling of these, through the same extent of the thermometrical scale, marked in seconds, was for the charcoal 937″, the lamp-black 1171″, and the wood-ashes 927″.

It appeared to Count Rumford, that the relative conducting powers of these substances are owing to the quantities of air inclosed in their interstices, and to the force of attraction by which this air is retained or confined. There can be little doubt, from observations I have afterwards to state, that air, when the motion of its parts is prevented, is a very imperfect conductor of caloric. If the imperfect conducting power of these substances, depended entirely on the difficulty with which caloric passes through their solid matter, then the relative degree of that power, would be as the quantity of that matter. Precisely the reverse, however, is the case. Count Rumford found, that by varying the state or arrangement of the same quantity of the same solid matter, the conducting power was considerably varied. The thermometer being surrounded with 16 grains of raw silk, the times of cooling from 70° to 10° of Reaumur amounted to

1284″; with ravellings of taffety 16 grains, 1169″; and with sewing silk cut 16 grains, 917″. Here it was obvious, that the more dense the same matter was, or the less air it contained, uniformly diffused through its interstices, the caloric passed with more celerity.

It is evident also, that the air remaining in the globe, in these experiments, if the motion of its parts had not been impeded, would have been sufficient of itself to have carried off the caloric much more quickly than it actually was. From the specific gravity of raw silk, it is shewn by Count Rumford, that the 16 grains of it in the globe, did not occupy more than $\frac{1}{55}$th part of the space in which it was confined, the rest of that space being filled with air. When the thermometer was surrounded merely with air, the time taken in cooling from 70° to 10° of Reaumur was 576 seconds; but when surrounded with raw silk, (the space occupied by the solid matter of that silk being 1, and by the air involved in it 54), the time of cooling was 1284″. Suppose, therefore, the matter of this silk to be even altogether incapable of conducting caloric, unless it had had some effect in preventing the air from carrying it off, its presence in the globe could only have prolonged the time of cooling, in proportion to the quantity of the air it had displaced, to the quantity remaining; that is, as 1 to 54, or a little more than 10 seconds. But the time of cooling was actually prolonged 708 seconds; and hence it is obvious, that the silk had greatly diminished the power which the air had, of carrying caloric from the heat-

ed thermometer. The mere mechanical intermixture of the fibres of silk, or similar substances, cannot alter the real conducting power of the air, or the property it has of communicating caloric from particle to particle, and their agency must therefore be referred to their power of impeding the motions of the mass of air by which the cooling of any body in contact with it is so much facilitated.

It is to be observed, however, that another circumstance must have operated in these experiments, and retarded the cooling of the thermometer. When a hot body is suspended in air, the radiation of caloric from it, by which its temperature is in part reduced, meets with no interruption; but any solid matter interrupts the calorific rays, and retains them. Hence the thermometer, when thus surrounded with the fibres of silk, would have its temperature more slowly reduced from this cause, or the caloric would escape more slowly, than when it was merely suspended in air.

There appears to be sufficient reason, from these experiments, to infer, that the imperfect conducting power of these substances will be proportioned to their sponginess, or the quantity of air they contain in their interstices, and the force of attraction with which that air is retained. That such an attraction exists, appears from the force with which they retain the air, which adheres to them even when immersed in water, or exposed under the exhausted receiver of the air-pump.

It is to this cause principally, that the property

which all light porous bodies, such as furs, feathers, wool and down, have of retarding the passage of caloric, is owing; and hence they form the warmest articles of clothing. On this also depends the imperfect conducting power of snow, which, in consequence of it, serves the important purpose of protecting vegetables from the severe winter cold.

When we wish to confine caloric, we of course avail ourselves of this difference in conducting power, and employ substances which are imperfect conductors. Thus furnaces are coated with a mixture of clay and sand, to prevent the dissipation of heat, and glass-vessels, which are to be exposed to heat, are covered in a similar way, to prevent the sudden alterations of temperature, by which the glass would be cracked.

To exclude caloric, or to prevent it from being communicated to a body from the surrounding medium, the same method must be employed,—surrounding the body with an imperfect conducting substance. On this principle ice-houses are constructed.

From the difference among bodies, in their power of conducting caloric, arise the differences in the sensations of heat and cold, which they excite when applied to our organs, though the thermometer discovers to us, that they are at the same temperature. The sensation of cold is produced by whatever abstracts caloric from the part to which it has been applied; and, of two bodies at the same temperature, the one which is the best conductor of caloric will abstract it most rapidly, and therefore occasion a more

intense sensation of cold. The sensation of heat is produced, when caloric is communicated to the sentient part; that body, therefore, which is the best conductor, will communicate a larger quantity in a given time, and therefore, when applied hot, will excite a greater sensation of heat than another will do at the same temperature, which is a less perfect conductor. Hence, a piece of metal, at a low temperature, feels much colder than a piece of wood, though their temperatures are proved to be the same by the thermometer; and on the contrary, it will at a high temperature feel much hotter than the other.

The preceding observations are applicable only to the conducting power of substances in the solid form. With regard to fluids, the mode in which caloric is distributed through their substance, so as to establish uniformity of temperature, is in part different, and Count Rumford advanced the opinion, that they are even perfect non-conductors, or altogether impermeable to this power.

When caloric is distributed over any mass of matter, we conceive of it as passing from one particle to another; and this constitutes what is termed the conducting power, this being more or less perfect, as the transmission of the caloric is more or less rapid. In this way, it was always imagined, that caloric might be distributed through fluids as well as solids; at the same time, it was obvious, that the diffusion of caloric through a mass of fluid was effected, partly at least, in another mode. The fluid, when heated, being ex-

panded, has its specific gravity diminished; from its mobility, the heated portion must rise to the surface of the mass; a new portion of fluid will come in contact with the part from which caloric is communicated, be heated, and rise in its turn; and thus the whole portion of fluid is brought successively into contact with that part; and these motions must continue, as long as caloric continues to be communicated.

In both these modes, was caloric conceived to be diffused through any mass of fluid, so as to raise the temperature of the whole to one point. The portion immediately heated, being expanded, rises to the surface; in its ascent, it was supposed to communicate part, at least, of the caloric it had received, to the particles with which it came in contact, and thus the temperature of the whole would be raised more quickly, than if the caloric were distributed merely by the successive application of different portions of the fluid to the heated surface. It was also supposed, that the conducting power of different fluids is very various, and experiments were instituted to ascertain these differences.

In opposition to this opinion, so conformable to what we know of the relations of caloric to matter, Count Rumford advanced the doctrine, that caloric is diffused over any mass of fluid in one of these modes only,—by circulation, or the motion and successive application of the fluid to the surface from which the caloric is communicated; and that the portion which is heated, imparts none of its caloric to the rest of the mass through which it ascends. "Although," says

he, "the particles of any fluid individually can re-
"ceive heat from other bodies, or communicate it to
"them; yet, among these particles themselves, all
"interchange and communication of heat is absolutely
"impossible."

Count Rumford was led to form this opinion, from having from time to time made several observations on the slowness with which caloric is distributed through fluids, when the motions of their parts are impeded; and his opinion was confirmed, by an accidental observation of an experiment in which the motions of a fluid, during change of temperature, was strikingly displayed. A large spirit thermometer, in which some fine particles of dust had been accidentally mixed with the fluid, had been placed in a situation in which it was exposed to the light of the sun; these particles, rendered more visible by this illumination, were observed moving with great rapidity in the tube of the thermometer, and by their motion, shewed the rapid currents of the fluid in the thermometer, produced by the heat communicated to it by the solar beams. One current rose in the axis of the tube, and another descended by its sides, a direction evidently owing to the heated particles going individually, and in succession, to give of their heat to the cold sides of the tube, and shewing the currents which are formed in a fluid while its temperature is rising. Count Rumford * imitated this accidental experiment, by diffusing in water a quantity of amber, in small

* Essays, vol. ii. p. 205.

fragments; increasing the specific gravity of the water, by dissolving a little potassa in it, until the fragments floated indifferently in any part of it, and then applying heat, when, as might have been foreseen, currents were formed, from the change in specific gravity of the heated portion of the fluid, and were rendered evident by the motion of the fragments of amber; the ascending current, as in the preceding experiment, occupying principally the axis of the vessel, and the descending currents being towards the sides, as there the temperature of the fluid was reduced by the transmission of caloric to the external air.

It is sufficiently evident, however, that although such experiments demonstrate that currents take place in a fluid which is heating; and although they establish, what indeed cannot otherwise be doubted of, that the fluid must have its temperature raised in a great measure, by the different parts of it coming successively into contact with the part through which the caloric is communicated; yet they are far from proving, that the fluid is heated solely in this mode. It is possible that the caloric received may in part at least be communicated from one portion of the fluid to another; and that this may have a share, even though we admit it to be a less considerable one, in raising the temperature of the whole mass.

Count Rumford, therefore, adduced some other facts to prove, that in fluids no such communication of caloric from particle to particle takes place. Of the greater number of his experiments on this sub-

ject, I conceive it unnecessary now to give any detailed account, but must refer to the Essays of the Author, Vol. II. Though greatly diversified, there are few of them but what are obviously inconclusive. Thus a series is given, in which it is shewn, that when the motions of a fluid are impeded, by dissolving in it any substance which renders it viscid, or by intermixing with it any imperfect conducting solid, the transmission of caloric through it is rendered very slow. But it is obvious, that this affords no proof, that fluids are non-conductors. No one can doubt but that the temperature of a fluid is rendered uniform, in some measure, by the motions of its parts. The question is, is this the sole cause? and such experiments as those now stated cannot establish this, since the diffusion of temperature over the mass of fluid, though rendered slower, still took place. In another series of experiments, it is attempted to be established, that caloric is not conveyed downwards through a fluid, and had this been made out, the opinion would have been established; for if a fluid be capable of communicating caloric from particle to particle, it ought to be transmitted through it in every direction; while, if the reverse is true, as no descending heated current can be formed, heat applied to the surface ought not to be conveyed downwards. But these experiments are still equally defective. It is only shewn, that caloric is conveyed downwards very slowly; — that ice, for example, fixed at the bottom of a glass jar, with warm-water above it, is melted more than eighty times slower than when it floats on the surface of

the water; as, in the latter situation, the water formed from the melting of the ice, being denser than the warm-water, descends, and allows fresh quantities of warm-water to be applied; while, in the former case, it remains interposed between the water and the ice, at least until the temperature of 40° is attained, when, from the anomaly in water already explained, in consequence of which it is more dense at some degrees above, than immediately at its freezing point a partial circulation is established. Accordingly, Count Rumford inferred, that were it not for this partial circulation, the ice at the bottom of the jar would not have been melted; and hence, that it would not be melted more quickly by water at a high temperature, than by water at 40°, a conclusion which he endeavoured to establish by experiment, but with results in some measure discordant, and requiring so many allowances for circumstances conceived to operate, as to be unsatisfactory. And had it even been established, it would not have been conclusive, as has been justly remarked by Mr Dalton *; for if caloric is communicated through fluids principally by the motion of their parts, as will not be questioned, water at 40° is at a more favourable temperature for melting ice than water at 60° or 80°, as, in the former, an ascending current will rise from the ice to the very surface, and a range of circulation be established through the whole column; while, in the latter

* Manchester Memoirs, vol. v. p. 395.

case, the ascending column will, at some part of the height, meet with water of its own density, when of course its ascent will be stopped, and thus the range of circulation will be comparatively limited. This advantage, which water at 40° has above water at a higher temperature, may more than compensate for the larger quantity of caloric which the latter might afford, by its directly conducting power. Hence, it might be admitted, what the general result of Count Rumford's experiments appear to establish, that even more ice is melted by water at 40°, than by an equal quantity of water at a much higher temperature, without the conclusion being established, that the melting of it is owing entirely to the circulation in the fluid; and as, in all the experiments, the ice actually did melt, it is obvious, that they cannot prove that fluids are non-conductors of caloric.

There is one experiment, however, which was made by Count Rumford, and which, as these sources of uncertainty were avoided, and as the result was more simple and decisive, appears to be more conclusive. Over a piece of ice, frozen in the bottom of a cylindrical glass jar, and having a small projection of ice rising from the centre of it, he poured olive oil at 32°, to the height of 3 inches above the surface of the ice, surrounding the under part of the jar with pounded ice and water. A solid cylinder of iron, $1\frac{1}{4}$ inch in diameter, and 12 inches long, to which a sheath of thick paper, to preserve its heat, was adapted, being heated to 210° by immersion in water, was introduced into the sheath, and suspended in the jar, in such a manner

that the middle of its lower extremity was directly above the pointed projection of ice, and distant from it only $\frac{2}{10}$ths of an inch. Did any heat, observes Count Rumford, descend through the thin stratum of oil which was interposed between the hot surface of the iron, and the pointed projection of ice under it, it must be apparent, by the melting of the ice, which would be discovered either by the diminution of the height of the projection, or by an alteration of its form. But this was not the case; the ice did not appear to be in the smallest degree diminished, or otherwise affected by the vicinity of the hot iron. The event was the same when mercury was substituted for oil, the iron being suspended in the mercury at the distance of $\frac{1}{4}$th inch from the projection of ice.

In this experiment, without any apparent, and, undoubtedly, without any intentional arrangement, the circumstances are still such as to occasion a waste of heat, and prevent any conducting power in the fluid, if it did exist, from being apparent. Instead of using only a small quantity of oil, the projection of ice was covered to a height of not less than 3 inches, and this oil was kept as nearly as possibly at 32°, during the whole of the experiment, by being surrounded, to the height of one inch above the level of the ice, by pounded ice and water. When the heated cylinder was suspended in the oil, the portion in contact with its sides, and the thin stratum immediately below its extremity, would receive caloric, be expanded, recede of course from the ice, and ascend; its place would be supplied by part of the oil above at 32°; and this

circulation would continue while caloric was communicated by the iron, the ascending current being in the middle, and the descending current by the cold sides of the jar; nor could it be prevented by the arrangement Count Rumford used, that of allowing the sheath to project about $\frac{1}{10}$th of an inch below the flat end of the iron, as, although this might confine a small quantity of fluid in contact with the iron, yet from the bottom of this, the current would still rise. In consequence of this circulation, it is obvious that no caloric could be communicated to the ice below, until the whole of this mass of fluid was heated above 32°. But when we consider its quantity, and that one inch of it was constantly surrounded with ice and water, it seems not improbable, that it could not be raised much above that temperature, from the quantity of caloric which the part of this cylinder of iron immersed in it could communicate. The mode of detecting the communication of caloric by the melting of the ice, was also very unfavourable, since, in that operation, a large quantity of caloric is absorbed, and a portion of caloric might be actually communicated to the ice, and yet might not be apparent, from the very small quantity it would be able to melt.

In opposition to Count Rumford's opinion, that fluids are non-conductors of caloric, a number of experiments have been made, by which, I believe, its fallacy is demonstrated.

At an early period, Dr Hope made some experiments with the view of investigating this subject. He found, that upon applying heat to the surface of wa-

ter in a vessel 11 inches in diameter, causing at the same time a stream of water to circulate on the outer side of the vessel, at the same height as the surface of the fluid within, to obviate the conducting power of its sides, caloric was conveyed downwards, as was discovered by the indications given by a thermometer beneath; and that, on mixing together portions of hot and cold water, and allowing the mixture, after agitation, to remain at rest, no separation took place, or the hotter portion of the fluid did not separate from the colder and more dense part, but the whole retained a uniform temperature;—results both of them inconsistent with Count Rumford's opinion *. Dr Thomson, in a very complete series of experiments, likewise found that caloric was conveyed downwards, both through water and quicksilver when heat was applied to their surface, a rise of temperature in various degrees being indicated by thermometers placed at different depths †. Experiments with a similar result were made by Mr Nicholson ‡; and Mr Dalton ascertained, by various experiments, the facts—that temperature is propagated downwards in fluids, and that portions of fluids at different temperatures, mixed together, attain a common temperature, which is preserved ‖. In some experiments

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* Transactions of the Royal Society of Edinburgh, vol. v. p. 394.

† Nicholson's Journal, 4to, vol. iv. p. 529.

‡ Ibid. vol. v. p. 197.

‖ Manchester Memoirs, vol. v. p. 373.

which I had made at an early period, of which I gave an abstract in my Elements of Chemistry, I likewise found that a fluid was always heated downwards when a hot body was placed at its upper surface, even when the jar containing the fluid was surrounded with water to obviate its conducting power.

It seemed to me afterwards, however, that whatever precaution of this kind is taken, we cannot be certain that the source of fallacy from the conducting power of the vessel is completely obviated. When heat is communicated to the surface of water, or any other fluid contained in a jar, the heated particles moving towards the sides must communicate caloric to the solid matter, which will in part be conveyed downwards, and again communicated to the cold water beneath; the water heated must thus ascend, and form a heated current rising from the sides, a descending current being necessarily formed in the axis of the vessel, a stratum of water thus indirectly heated will be constantly accumulating, by which the thermometer, sooner or later, according to its distance, will be affected. Nor can this source of uncertainty be completely removed by surrounding the jar externally with water, a method which I employed in my first experiments; for although part of the caloric conveyed downwards by the sides of the vessel will be abstracted by this external water, as I found to be the case from its temperature being raised, yet another part must equally be given to the fluid within the vessel; nor is it possible to determine with any accuracy what proportions of the caloric which the

vessel conveys are given off at its external, and at its internal surface, so as to make any due allowance for its effect in the experiment. Any other precaution, too, which we can take to guard against this source of inaccuracy, such as employing a wide vessel, or interposing a great depth of fluid between the thermometer and the body communicating caloric, defeats the purpose of the experiment itself, since such precautions, while they no doubt lessen the effect from the communication of caloric by the vessel, lessen equally the effect which would result from a conducting power in the fluid, if it do possess it; and therefore it must remain uncertain to what the diminished effect which always takes place where they are employed is to be abscribed.

It at length occurred to me, that this source of uncertainty might be completely obviated by a very simple contrivance; employing a vessel of ice in which a fluid at 32° should be placed. Ice cannot possibly have its temperature raised above 32° of Fahrenheit; for if caloric be communicated to it, it is spent merely in melting it. Hence it cannot communicate any temperature above that point, and of course, if a fluid contained in a vessel of ice be heated downwards, by a hot body applied to its surface, we may conclude with certainty that the caloric has been conveyed by the conducting power of the fluid.

For an account of the manner in which the experiment was made, with the necessary precautions, I must refer to Nicholson's Journal *. In a hollow cy-

* Nicholson's Journal, 8vo, vol. i. p. 241.

linder of ice, a thermometer was placed horizontally, at the depth of one inch, its bulb being in the axis of the cylinder, and the part of the stem to which the scale was attached entirely without. As water could not be employed at the temperature at which it is requisite to make the experiment in this apparatus, on account of the property it possesses of becoming more dense in the rise of its temperature from 32° to 40°, oil was first used. A quantity of clear almond oil, at the temperature of 32°, was poured into the ice cylinder, so as to cover the bulb of the thermometer $\frac{1}{2}$ inch. A flat bottomed iron cup was suspended, so as merely to touch the surface of the oil, and two ounces of boiling water were poured into it. In a minute and a half, the thermometer had risen from 32° to 32° $\frac{3}{4}$; in 3 minutes, to 34° $\frac{1}{2}$; in 5 minutes, to 36° $\frac{1}{4}$; in 7 minutes, to 37° $\frac{1}{4}$, when it became stationary, and soon began to fall. When more oil was interposed between the bottom of the cup and the bulb of the thermometer, the rise was less; but even when its depth was three quarters of an inch, the rise was perfectly perceptible, amounting to 1$\frac{1}{2}$ degree. With mercury the same results were obtained, the thermometer rising only with much more rapidity, from the mercury being a better conductor than the oil.

These experiments I would regard as decisive, in establishing the conducting power of fluids. The source of error from the sides of the vessel is entirely obviated; no currents could be formed, by which the rise of the thermometer could be occasioned, nor is there any mode in which that effect could have been

produced, but by the fluid conducting the caloric from particle to particle.

Still we have every reason to believe that fluids are very imperfect conductors of caloric, and that the distribution of caloric through them is in a great measure by the circulation of their parts; for we find, that when this is impeded or prevented, the communication is extremely slow. It has been stated, as proved by Count Rumford, that ice is melted eighty times slower when at the bottom of a column of water, than when floating on its surface; and, if we exclude the partial circulation, which even in the former case takes place, from the increased density of the water, as it is heated from 32° to 40°, and from the influence of the containing vessel, the difference must be still more considerable, and amply demonstrates the very imperfect conducting power of the fluid.

It is difficult to ascertain with precision the relative conducting powers of different fluids, because it is difficult to discover what proportion their real conducting power bears to that mobility by which a more or less rapid circulation of their parts takes place, when they are subjected to a heating or cooling cause, and by which uniformity of temperature through them is chiefly established. In the experiments I have stated, mercury appears to be a much better conductor of caloric than oil or water, as the thermometer immersed in it rose with much greater rapidity when a hot body was applied to the surface. This difference is even conspicuous in the different intensity

of sensation which these fluids occasion. Count Rumford, in his early experiments on the conducting powers of bodies, found, that when the thermometer was surrounded with quicksilver, it required to raise it to a certain extent of temperature, immersion in boiling water for $36\frac{2}{3}$ seconds, while, when surrounded with water, the time requisite for raising it the same extent was 1.57, or 117 seconds *. Hence the conducting power of quicksilver is to that of water, according to these experiments, as $36\frac{2}{3}$ to 117 inversely, or directly as 1000 to 313. But it is still to be remarked, that though this may approach to the real difference between them in conducting power, it may not express it with perfect accuracy, as the rapidity with which caloric will be distributed through them must be proportioned not only to this power, but must be dependent also on the greater or less mobility of the fluid, and on the degree of expansion which each suffers from the communication of a given quantity of caloric. The more a fluid is expanded by a given change of temperature, the greater will be the difference in specific gravity between the part which is heated, and the rest of the mass; and the more rapid therefore will be the circulation from this change of specific gravity. The less tenacity or viscosity, also, a fluid has, it is evident its parts will move with more facility. And it cannot be doubted, but that fluids may, and actually do differ in these as well as in their conducting powers. Yet, even allowing for

* Essays, vol. ii. p. 425.

these, we can in some cases discover the predominance of the real conducting power, though we may be unable to ascertain its extent with perfect accuracy. Thus quicksilver suffers less expansion from a given change of temperature, than alkohol does, and therefore, while receiving caloric, the internal circulation of its parts must be less rapid, as there will be less difference of specific gravity between the portion heated and that which is not; and we have no reason to believe that quicksilver is more mobile than alkohol; yet we find that quicksilver takes the temperature of the surrounding medium much more quickly than alkohol, as is evident from the greater delicacy of the mercurial than the spirit thermometer. This, of course, proves a superiority in the proper conducting power.

My friend Dr Traill, who has added some arguments to those before stated against Count Rumford's conclusions as to the non-conducting power of fluids, as well as to the reasoning by which he has more lately endeavoured to support his opinion, has given some experiments on the relative conducting powers of different liquids, more extensive than any we have. They were performed by ascertaining the times which were requisite to raise a mercurial thermometer, placed in the liquid submitted to trial, 3 degrees of Fahrenheit, in consequence of the transmission of caloric downwards, from the extremity of a cylinder of iron, one inch in diameter, heated to 212°, and suspended in the liquid so as be distant from the bulb of the thermometer 0.5 inch, the vessel being of wood, to ob-

viate as much as possible any effect from its conducting power. The results are given in the following table *:

	Liquids.	Minutes.	Seconds.
1.	Mercury, - -	0	15
2.	Saturated Solution of Sulphate of Soda,	6	30
3.	Water, - -	7	5
4.	Proof Spirit, -	8 nearly	
5.	Solution of Sulphate of Iron, one part of Salt to five of Water,	8	0
6.	Water of Potassa, -	8	15
7.	Milk of a Cow, -	8	25
8.	Saturated Solution of Sulphate of Alumine,	9	40
9.	Transparent Olive Oil,	9	50
10.	Alkohol. Lond. Pharm.	10	45
11.	Saturated Solution of Sulphate of Soda, but the Liquid not touching the Iron Cylinder by 0.1 inch, or *nearly so*, - - -	19	20

From the manner of executing these experiments, no important influence can be ascribed to any circumstance, independent of the proper conducting power of the liquids, as little effect could be produced by any differences which might exist in expansibility or mobility; nor can the results be accounted for on any differences of this kind. They must, therefore, be regarded as nearly indicating the different conducting powers.

* Nicholson's Journal, vol. xii. p. 137.

Count Rumford advanced the same opinion with regard to airs as with regard to non-elastic fluids. He considered them as non-conductors of caloric, and supposed, that the change of temperature which any body in the aërial form suffers, arises entirely from the motion of its parts produced by the alteration in specific gravity which the communication of caloric occasions. The experiments by which he endeavoured to support this opinion are of a similar nature to those from which the non-conducting power of liquids was inferred, principally shewing, that whatever obstructs the motions of a mass of air, renders the propagation of caloric through it much more slow. They are even, from the greater difficulties which attend the execution of them, less satisfactory than those on liquids. And the same conclusion is probably to be drawn as to the general question. The reason why a fluid conducts caloric so slowly, is apparently, that, from the mobility of its parts, as soon as a particle is heated it recedes from the others, and does not communicate the caloric it had received. The same cause, we might be disposed to conclude, must operate in the aëriform fluids, and render them very imperfect conductors, though there seems little probability in the conclusion, that they are altogether incapable of conducting caloric.

We observe even that different bodies in the aërial form conduct caloric with different degrees of celerity, and that these differences cannot be ascribed to any difference in their facility of being put in motion. The most striking example of this which we have is

in air which is dry, compared with air loaded with moisture. In some experiments which Count Rumford made, prior to the time when he had fully adopted the opinion of aëriform bodies being non-conductors, he found, that a thermometer surrounded with humid air was much more rapidly heated when exposed to a source of caloric than when it was surrounded with air perfectly dry, the time required to raise it in dry air from the temperature of freezing to nearly that of boiling water, by plunging the vessel containing it into the latter fluid, being 8 minutes 9 seconds; while, in moist air, it required only 1 minute 51 seconds, a difference as 330 to 80 *; though, as Pictet has remarked, there is a source of fallacy in the experiment, from the circumstance, that to render the air humid, the sides of the vessel were merely wetted with water, which, when converted into vapour, would again condense in part on the cold bulb of the thermometer, and by the latent heat it would give out, would contribute to raise its temperature; and accordingly, in the reverse mode of making the experiment, or observing the time the thermometer takes to cool in dry and humid air, the difference does not appear so considerable. Some difference in conducting power is even obvious, however, in the effects of air in these states on our sensations; damp air when at a moderate or rather low temperature, feeling much colder than air at the same temperature which is perfectly dry. Count Rumford, in the same

* Essays, vol. ii. p. 417.

series of experiments, did not find much difference in the conducting power of the same air at different degrees of density.

Berthollet, I must remark, however, has advanced the opinion for which there seems to be some grounds, that aëriform fluids, so far from being imperfect conductors of caloric, conduct it with great rapidity. The familiar example of the celerity with which an air thermometer indicates the slightest change of temperature, is mentioned by him as a proof of the great celerity with which air receives caloric from another body. He also mentions the fact, that aërostats have sometimes experienced a sudden dilatation of the air in their balloon, from the appearance of the sun. He remarks, apparently with justice, that the particles of the contained air cannot be supposed to take the increased temperature which the expansion indicates, by being brought individually, and of course successively, to the covering of the balloon; and still more, that the lower particles, which are contiguous to that portion of the covering which does not receive the solar beams, cannot be heated in this manner. Hence, he concludes, that these phenomena indicate, that the elastic fluids, far from being imperfect conductors, receive the temperature of others very quickly *. The fact which Count Rumford's experiments appear to establish, that air, when confined, impedes the communication of caloric, he supposes to be owing to the state of compression in which it exists, by which its

* Chemical Statics, vol. i. p. 465.

dilatation is prevented, and this opposes an obstacle to the caloric diffusing itself. One fact seems adverse to this theory, which Rumford himself ascertained, and which has been already stated, that there is little difference in the conducting power of condensed and rarified air. At the same time, as the cooling of a body in air is effected probably more by the radiation of caloric from it than by the slow communication, it is probable there might be even a considerable difference in the conducting power of dense and rarified air, without the difference being very apparent in the time of cooling in Rumford's experiments.

In concluding this subject, I may briefly observe, that it is principally by the agency of fluids, elastic and non-elastic, that the distribution of caloric over the globe is regulated, and great inequalities of temperature guarded against; and that this agency is even exerted chiefly by the circulation of their parts, of which their mobility renders them susceptible.

Thus, the atmosphere with which the earth is surrounded, serves the important purpose of moderating the extremes of temperature in every climate. When the earth is much heated by the sun's rays, the stratum of air immediately reposing on it receives part of its caloric, is rarified, and ascends; its place is supplied by colder air pressing in from every side; and, by this constant succession, the heat is moderated that would otherwise become intense. This warm air is, by the pressure of the constant ascending portions, forced towards a colder climate, where it serves to moderate the extremes of cold. There thus flow a

current from the poles towards the equator, at the surface of the earth, and no doubt another superior current from the equator to the poles; and though the directions of these are variously changed, by inequalities of the earth's surface, they can never be interrupted, but produced by general causes must always operate, and preserve more uniform the temperature of the globe.

Water is not less useful in this respect in the economy of nature. When a current of cold air passes over the surface of a large collection of water, it receives from it a quantity of caloric; the specific gravity of the water is increased, and the cooled portion sinks. Its descent forces up a portion of warmer water to the surface, which again communicates a quantity of caloric to the air passing over it; and this process may be continued for a considerable time, proportioned to the depth of the water: If this is not very considerable, the whole is at length cooled to 40°, below which, the specific gravity not increasing, the circulation ceases, and the surface is at length so far cooled as to be covered with ice. If, on the contrary, the depth is much greater, the application of the cold air may be continued much longer without this result; and in this, and many other countries not intensely cold, it often happens that deep lakes are not frozen in the course of the winter. The depth of the ocean being still greater, and the body of water larger, while, at the same time, from its saline matter, its points, both of freezing and maximum density, are

lowered, it resists freezing still more effectually, and is scarcely frozen indeed except in the polar regions.

The quantity of caloric thus communicated by water is exceedingly great. The heat, says Count Rumford, " given off to the air by each superficial foot of water, in cooling *one* degree, is sufficient to heat an incumbent stratum of air 44 times as thick as the depth of the water, 10 degrees. Hence we see how very powerfully the water of the ocean, which is never frozen over except in very high latitudes, must contribute to warm the cold air which flows in from the polar regions."

Count Rumford supposes, and with good reason, that currents exist in the ocean similar to those formed in the atmosphere. The water which, in the colder regions, is cooled at the surface, descends, and spreading on the bottom of the sea, flows towards the equator, which must produce a current at the surface, in an opposite direction; and thus the ocean may be useful in moderating the excessive heats of the torrid zone, as well as in obviating the intense colds of the polar regions.

RADIATION OF CALORIC.

I HAVE remarked, in the beginning of the present section, that caloric is propagated or diffused over matter, not only by slow communication, but that, from a body at a high temperature, it is likewise projected in right lines, which move with great velocity, and obey the same laws of motion as the rays of light. This constitutes its Radiation, the subject I have now to consider.

This property of caloric, though scarcely attended to until within these few years, had not altogether escaped observation. In the Memoirs of the Academy of Sciences for 1682, is an experiment of Mariotte, in which it is pointed out. "The heat of a fire," it is said, "reflected by a burning mirror, is sensible in "its focus; but if a glass be interposed between "the mirror and the focus, the heat is no longer sen-"sible *."

Lambert made a similar experiment, and still more clearly shewed, that the heat produced is not owing to the agency of light. Finding, that from burning charcoal, placed properly between two concave mirrors, such a heat was produced, as to kindle a combustible body at the distance of 20 or 24 feet; to discover whether this arose from the light emitted, he collected, in the focus of a large lens, the light of a clear burning fire, but found it to have scarcely any heat sensible to the hand †.

Scheele, in his Treatise on Air and Fire, alludes to these experiments, in which heat is excited at a distance, by the reflection and concentration of this calorific matter, and he added several new and very important observations with regard to it. He shewed, that this radiant heat, as he named it, passes through the air without heating it, and that any current in the

* *Voyages dans les Alpes, par Saussure*, t. iv. p. 140.

† Ibid, p. 119.

atmosphere does not change its direction. If a pane of glass be interposed between the fire emitting it and the hand, it is completely arrested, and no sensation of heat is received, though the light from the fire is transmitted, and may be concentrated by a mirror, so as to form a bright focus, but without any heat. A glass mirror, he observes, though it reflects the light of a fire, does not reflect the heat, but absorbs and retains it, while a polished metallic surface reflects this radiant heat, as well as the light. A metallic mirror, therefore, opposed to a source of heat, may be held a long time without becoming warm. But he adds, that if this mirror be blackened, by holding it over a burning candle, it cannot be kept four minutes in the hand, opposed to a fire, without exciting too strong a heat to allow it to be held *. The general facts, for which we are indebted to Scheele, and which form the greater part of what has yet been discovered on this subject, are, That radiant caloric is reflected from metallic surfaces, but is absorbed, and not reflected or transmitted by a glass;—that when a metallic surface is blackened, it no longer reflects, but absorbs, and becomes therefore much sooner heated; that radiant caloric moves with velocity through air, undisturbed by any motion of the air, and without appearing to communicate to it any increase of temperature; and that, when associated with light, it can be separated from it, so as to obtain the peculiar effects of each apart from the other.

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* Experiments on Air and Fire, p. 67—71.

Saussure, in endeavouring to discover the cause of the cold that prevails on the summit of high mountains, was led to attend to the experiment of Lambert, and, in conjunction with Pictet, repeated and varied it. The apparatus they employed consisted of two concave mirrors of tin, moderately polished, a foot in diameter, with a focus of $4\frac{1}{2}$ inches. These were placed opposite to each other at the distance of 12 feet 2 inches. In the focus of one of them was the bulb of a mercurial thermometer, in that of the other was put a ball of iron, 2 inches in diameter, which had been raised to a red heat, and allowed to cool, until it was no longer luminous even in the dark. The moment the ball was introduced, the thermometer in the opposite focus began to rise, and in six minutes it had risen from 4 degrees to $14\frac{1}{2}$ of Reaumur's scale, while another thermometer, suspended without the focus, but at the same distance from the heated ball, rose only from 4° to $6°\frac{1}{4}$. This experiment was often repeated, and always with the same result *. It proves, that a matter is projected in right lines from heated bodies, capable of raising the temperature of any substance by which it is interrupted. The rationale of the experiment is sufficiently obvious. The heated body emits rays of caloric in right lines, those of them which proceed towards the mirror, in the focus of which it is placed, are reflected and projected on the surface of the opposite mirror; from it they are again reflected, and though

* *Voyages dans les Alpes*, t. iv. p. 120.

at each surface some are lost, yet a sufficient number are united in the focus to produce a considerable effect on the thermometer, while the thermometer without the focus receives only the few direct rays from the surface of the sphere, equal to its own surface, to which it is opposed.

Pictet prosecuted these experiments. In substituting a burning candle instead of the heated ball, the thermometer rose, in one experiment, from 4.6 degrees to 14°, in another, from 4.2 to 14.3 *.

In both experiments there was some ground for the suspicion, that light, which moves in right lines, might give rise to much, or perhaps even to the whole of the effect. From the burning candle it would be copiously emitted; and though the heated ball did not appear luminous even in the dark, this might be ascribed to the imperfection of vision; and as the temperature was so near to that of ignition, it might be supposed that its agency was still to be ascribed to light. Pictet repeated the experiment which had before been made, but with more accuracy,—that of interposing a plate of glass between the radiating body and the thermometer, which would afford a ready passage to any light present, while, if the rays were of the nature of caloric, these might be expected to be intercepted. When the burning candle had been placed in the focus, and had raised the thermometer in the opposite focus from 2 to 12 degrees, a plate of very transparent glass

* *Essais de Physique*, p. 63.

was interposed, and in 9 minutes the thermometer had descended to 5.7, that is more than one-half. On removing the glass, the thermometer immediately rose. Even the effect which was produced while it was interposed, is probably not to be ascribed to the agency of light, but partly to the rays of caloric being imperfectly intercepted, and partly to the glass itself being heated by those which were arrested, and thus becoming a source of radiating caloric. He performed another experiment, in which the operation of light cannot be suspected. A glass matrass, capable of containing rather more than two ounces by measure, was filled with boiling water, and placed in the focus of one of the mirrors. The other was placed at the distance of 10 feet 6 inches, and in its focus was suspended a small mercurial thermometer, having Fahrenheit's scale. This in two minutes rose from 47° to $50°\frac{1}{8}$; and when the matrass was removed, it instantly began to fall. These experiments leave no room to doubt of the radiation of caloric, as they prove, that a calorific matter is projected in right lines from bodies the temperature of which is moderately raised.

It is known, that when bodies are blackened, they are more heated by the rays of light than when they are not so prepared. From the experiments of Scheele, in which he blackened the metallic mirror placed before a fire, and found it was soon much more heated than when clean, it appeared to be the same with regard to radiant caloric; and this was unequivocally ascertained by Pictet. When the bulb of the thermometer employed in the last experiment, and which, by the ca-

loric radiated from the matrass of boiling water was raised from 47° to 50°$\frac{1}{8}$, was blackened, it rose, the experiment being in every other respect the same, from 51°$\frac{1}{8}$ to 55°$\frac{1}{4}$.

From Scheele's experiments might be collected, though with some obscurity, the effect of different kinds of matter at the same temperature, in radiating caloric. Experiments of a similar nature, though likewise obscure as to their rationale at that time, were made by Pictet, by interposing a glass mirror or plate, covered with amalgam on one side, between the hot body and the thermometer, and according as the glass or the metallic surface was opposed to the hot body, or according as either surface was blackened, the calorific effect on the thermometer was different; the effect being least, or as 0.5, when the glass surface was opposed to the hot body, and the metallic one of course to the thermometer, while, in the opposite arrangement, or with the metallic surface opposed to the hot body, and the glass surface to the thermometer, it was as 3.5; when the metallic surface opposed to the source of heat was blackened, the calorific effect on the thermometer was as 9.2, and when the coat of amalgam was entirely removed, and the glass surface opposed to the hot body blackened, it was not less than 18° *.

In employing a concave glass mirror, placing it behind the thermometer, scarcely any rise was indicated, even although a heated ball of tin was opposed to it,—a very simple experiment, by which the different powers

* *Essais*, p. 72.

of glass and metal in reflecting caloric, is also demonstrated.

Pictet, though he made the experiment, could not ascertain whether this radiating calorific matter suffered refraction. He endeavoured, but by a very rude experiment, to discover the velocity of its motion. Two concave mirrors were placed at the distance from each other of 69 feet; at the distance of a few inches from the focus of the mirror, in which the heated body was to be placed, a thick skreen was suspended, the air thermometer being placed in the focus of the other mirror. The ball of iron which had been used in these experiments, heated somewhat below ignition being introduced, the skreen was withdrawn. At that instant the thermometer rose, nor was it possible to perceive an interval of time between its rise and the lifting of the skreen. The moment the skreen was dropped, the ascent of the thermometer ceased. From the velocity with which radiant caloric passes through the atmosphere, it does not raise its temperature, as was remarked by Scheele.

After these experiments by Saussure and Pictet, on the radiation of caloric, had been published, the subject was not prosecuted for several years. At length Herschel, in his investigation of the constitution of the solar ray, made the important discovery, that radiant caloric is a constituent part of it, being associated with visible light. He was led to this discovery by finding, that when a solar ray is decomposed by the prism, the different coloured rays have very different heating powers; the most refrangible of the visible rays, the indigo,

is least powerful in exciting heat, and the calorific power increases towards the other side of the spectrum, and is greatest in the red rays. This was ascertained by receiving the prismatic spectrum on a piece of pasteboard, in which was an opening of sufficient length to allow the whole of one of the prismatic colours to pass through. Very sensible thermometers were placed beneath, and by the rise they suffered, the heating powers of the different rays were compared *.

He further found, however, that besides the distribution of calorific rays in different proportions among the visible rays, they exist entirely apart from it, and beyond that side of the visible prismatic spectrum bounded by the red rays. The maximum of heating power is about half an inch beyond the visible light, but it can be traced to the extent even of an inch and a half. This must be received as a proof of the existence of radiant caloric in the solar beam. The former appearances might perhaps be accounted for by supposing light to have, as a property belonging to it, the power of heating bodies, and that this property is possessed by the different rays in different degrees of intensity. But when we find that rays are separated by the prism, still more powerfully heating, but altogether invisible, and incapable of being brought to excite any illumination, we must regard this as a proof sufficiently decisive of the presence of radiant caloric. This discovery, with regard to the different heating powers of the different coloured rays, and the existence

* Philosophical Transactions for 1800, p. 257.

of an invisible calorific matter, has been confirmed, as I shall have to state more fully in the history of Light, by Sir H. Englefield, by experiments even more unexceptionable, in some respects, than those of Herschel.

The phenomena of the experiment now stated, prove radiant caloric, at least as it exists in the solar rays, to be liable to refraction, since it is separated by the prism from the rays of visible light, or, in being transmitted through it, is turned aside from the direction in which it was moving. It appears even that a beam of radiant caloric must consist of rays of different degrees of refrangibility. The experiments shew, that the calorific rays are dispersed over a space even greater than that occupied by the visible rays of light. If the radiant caloric existing in the sun beam were not refrangible, it would fall upon an equal space, in the place where the shadow of the prism, when covered, may be seen; and if various degrees of refrangibility did not belong to it, it must fall uniformly on a space equal to the area of the prism. But neither of these being the case, the conclusions may be drawn, that radiant caloric is subject to the laws of refraction, and also to those of the different refrangibility of light; and that the range of its refrangibility is even more extensive than that of the coloured rays.

Herschel made the interesting experiment, of ascertaining whether the radiant caloric projected from heated bodies, is likewise refrangible. By placing a lens at a small distance from a burning candle, with a pasteboard skreen, having an aperture of nearly the

same size as the lens interposed, the direct rays from the candle, which passed through this aperture, were refracted by the lens, and thrown on a thermometer in its focus, which was thus raised in three minutes $2\frac{1}{2}$ degrees *. A similar experiment was performed on the calorific rays issuing from a common fire, from a mass of red-hot iron, and likewise from iron heated, but not to ignition; and the results equally proved, that these rays are subject to the laws of refraction. He also subjected to experiment the invisible calorific rays of the solar beam, and found that they were accurately refracted to the focus of the lens †.

Radiant caloric, whether existing in the rays of the sun, or emanated from heated bodies, and whether connected with visible light or not, he likewise proved to be subject to the usual laws of reflection. He employed a single concave metallic mirror of $3\frac{4}{10}$ inches diameter, and placed it at the distance of 29 inches from a candle. The ball of a thermometer being placed in its secondary focus, the rise of temperature which it indicated was, in five minutes, $3\frac{1}{4}$th degrees from the reflected rays; another thermometer, placed near, but out of the reach of reflection, not being at all affected ‡. Similar experiments, and with the same general results, were made on the calorific rays from steel red-hot; from a coal fire; and from an iron stove, or a rod of iron, at a heat inferior to

* Philosophical Transactions, 1800, p. 272.; Ibid. p. 309.

† Ibid. p. 317. ‡ Ibid. p. 297.

that of ignition *. The radiant caloric existing in the rays of the sun, either associated with the visible light, or separated from it by the prism, were found, by similar experiments, to be likewise susceptible of reflection and condensation †.

So far the radiant caloric which exists in the solar rays, and that which is emitted from bodies at a high temperature, agree in their properties. It follows, however, from Herschel's experiments, that a difference exists between them in one property, that of passing through transparent media, the latter being transmitted with much more difficulty than that which exists in solar light.

The apparatus employed to ascertain this, consisted of two thermometers of equal sensibility, the one being covered with glass or some other transparent substance, the other remaining uncovered, and both, with the requisite precautions, being exposed to the operation of radiant caloric ‡.

In the first experiment, they were equally exposed to the solar rays, a piece of glass, very transparent, and of a bluish white tinge, covering the one. This thermometer, in five minutes, rose from 67° to 71° ½, while the uncovered one rose in the same time from 67° to 73° ‖. Here, therefore, one-fourth of the radiant caloric was intercepted; or, if we suppose 1000

* Philosophical Transactions, 1803, p. 305-6.

† Ibid. p. 298. 302—4. ‡ Ibid. p. 446.

‖ P. 450.

rays to have impinged on the glass, 750 were transmitted, and 250 stopped. When a piece of flint glass, about $2\frac{1}{2}$ tenths of an inch thick, covered the thermometer, it rose in five minutes 5 degrees, while the other, in the same time, rose $5^{\circ}\frac{1}{2}$, or of 1000 incident rays of radiant caloric, only 91 were intercepted by the glass *.

The experiment was repeated, by exposing the thermometers, as before, to the rays from a burning candle. The uncovered thermometer rose in five minutes from $59^{\circ}\frac{3}{8}$ths to $62^{\circ}\frac{2}{8}$ths; the other, covered with the bluish white glass, from $59^{\circ}\frac{1}{2}$ to $60^{\circ}\frac{5}{8}$ths. Here more than half of the calorific rays were intercepted, or of 1000, 375 were transmitted, 625 stopped. When the experiment was repeated with the piece of flint glass, the one thermometer rose in five minutes from $59^{\circ}\frac{7}{8}$ths to $62^{\circ}\frac{5}{8}$ths; the other, from $59^{\circ}\frac{5}{8}$ths to $60^{\circ}\frac{3}{4}$ths, or of 1000 incident calorific rays, 409 passed through, 591 were stopped †. It is thus obvious, that the radiant caloric from burning bodies passes with much more difficulty through glass than the radiant caloric existing in the rays of the sun.

In both these sets of experiments, the radiant caloric was connected with light, which might perhaps influence its transmission through the glass. But we have experiments with the calorific matter alone, by which this may be determined.

The radiant caloric, or invisible heating rays in the

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* Philosophical Transactions, 1803, p. 451.

† Ibid. p. 464.

solar rays, being separated from the illuminating rays, the thermometers were exposed to the former; in five minutes the uncovered thermometer rose from 48° to 49° $\frac{3}{4}$ths; the other, covered with the bluish white glass from 47° to 48° $\frac{5}{8}$ths, or of 1000 rays, only 71 were stopped; and when the piece of flint glass was used, the rise was equal, or no rays appeared to be arrested *. The experiment was also performed on the radiant caloric emanated from a body heated, but not luminous, generally from an iron stove. In three minutes the uncovered thermometer rose from 56° to 59° $\frac{3}{4}$ths; the other, covered with the bluish white glass, from 55° $\frac{3}{4}$ths to 56° $\frac{7}{8}$ths, consequently considerably less than the half was transmitted, or of 1000 rays, 700 were stopped. On employing the piece of flint glass, the proportion of rays arrested was 533 †. When other transparent colourless substances, as Iceland crystal, or talc (mica probably), were used, the general results were similar to those with the glass.

These experiments leave no doubt as to the more difficult transmission of the radiant caloric from heated bodies through transparent glass, and of course point out a difference between it and the radiant caloric which exists in the solar rays. We might perceive, indeed, this difference from familiar facts. We know that when a piece of glass is interposed between a heated body, placed in the focus of one mirror, and a thermometer in that of the other, the ra-

* Philosophical Transactions, 1803, p. 485.

† Ibid. p. 492.

diant caloric is nearly completely intercepted ; while, on the other hand, we also know, that when the solar rays are concentrated by a lens, a very intense heat is excited in its focus, a sufficient proof that the radiant caloric, or the greater part of it, existing in these rays, passes through the glass.

Herschel also examined the powers of differently coloured glasses, in intercepting both these varieties of radiant caloric ; but his experiments on this subject are too numerous to be detailed ; and I must refer, therefore, to the memoir itself. In general, the coloured glasses intercepted much more of the radiant caloric than the uncoloured, whether that from the sun or that from heated bodies. One singularity is to be observed, that these coloured glasses intercept more of the radiant caloric of the solar rays when this is connected with light ; in other words, when the entire solar ray is made to impinge on the glass, than they do of the radiant caloric from heated bodies ; but, on the other hand, when the radiant caloric of the solar ray is separated from the visible light, much less of it is intercepted than of the other. Even the calorific rays of the different orders of refrangibility in the solar beam, possess, in very different degrees, the power of passing through different substances *.

In ascertaining the capability of solar radiant caloric of passing through fluids, Dr Herschel found, that of 1000 rays incident on a tube containing water, 558

* Philosoph. Trans. 1803, p. 453-4, 465-6, 486-7. 493.

were stopped; and on one containing alkohol, 612; but it is not easy to ascertain what portion was intercepted by the glass, and what by the liquid *. It has been already shewn, that the radiant caloric from heated bodies is scarcely capable of penetrating liquids. In the experiment I performed on the conducting power of fluids in the ice vessel, when the heated iron ball was suspended over transparent almond oil, so *as not to touch it*, the thermometer beneath was scarcely affected, which it would have been had the rays of caloric penetrated the liquid with facility; and, on the other hand, when the ball did touch the liquid, so as to admit of the slow communication of caloric, the thermometer rose in 20 minutes 9 degrees.

Dr Herschel's views, in making these experiments, were directed to a different object than the comparison of the properties of these varieties of radiant caloric; the experiments being designed principally, as I shall afterwards have to state, to prove that the heating and illuminating powers of the visible rays of light do not depend on one set of rays; but the one on rays of light properly speaking, the other on rays of caloric. Hence he scarcely attends to the differences I have pointed out in the above abstract. They follow, however, directly from his experiments, and are results highly interesting.

I have now to give an abstract of the important experiments of Mr Leslie, contrived with much inge-

* Philosophical Transactions, 1803, p. 457.

nuity, and executed by an apparatus simple, but well adapted to display the phenomena of radiant caloric, and to admit of their accurate examination. He employed a single reflecting mirror of tinned iron, highly polished, placed upright in a small wooden frame. As the substance radiating caloric, he employed small hollow cubes of tin, from three to ten inches, which were filled with hot water, and placed before the mirror at the distance of a few feet; and, by covering or preparing the sides of the cube in various ways, he could without any difficulty ascertain accurately the effect of different kinds of matter on the radiation *.

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* To measure the effect in these experiments, Mr Leslie employed the instrument which he invented, the differential thermometer, which combines great delicacy with accuracy. It is an air-thermometer, but instead of being merely a cylindrical tube, with one ball, it has two equal bulbs, one at each extremity of the tube, and this tube is bent into the shape nearly of the letter U. Previous to connecting the balls with the tube, by the blowpipe, a small quantity of coloured liquor (sulphuric acid tinged with carmine,) is introduced, so as to fill the curved part of the tube, and rise to a certain height in each of the legs, which, to admit of a sufficient range are from three to six inches long. The curved part of the tube is then fixed in a small wooden frame, so as to admit of the instrument standing in a vertical position. The principle which gives it accuracy, is, that it is not at all influenced by any variation of temperature in the surrounding medium. When both balls are at the same temperature,

The tin cubical vessel being filled with boiling water, and placed before the reflector, a few feet distant, and one of the balls of the differential thermometer being placed in the focus of the mirror, a rise of temperature is immediately indicated, or the liquor descends in the leg connected with this ball, and rises in the other.

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the elasticity of the air in the one being equal to that in the other, the liquor in each tube or leg will be equally pressed on, and will remain stationary at a certain height. If the instrument be introduced into either a warmer or colder atmosphere, the temperature of both balls will be equally affected; the volume of air in each will be equally expanded or contracted; and hence the liquor will still remain stationary. But, if one of the balls be more heated or cooled than the other, this equilibrium is subverted, and the liquor must rise in the tube connected with the ball which is at the lower temperature, and of course fall in the other. Hence the instrument is calculated to point out the *difference* of temperature in the corresponding balls; it will do so with much sensibility; and on both accounts is peculiarly calculated for experiments on radiant caloric. A scale is of course attached to one of the legs of the instrument, by which the rise or fall can be measured with accuracy. The scale Mr Leslie employed, was formed by dividing the interval between freezing and boiling water into 100 degrees, and subdividing each of these decimally, these last divisions being the degrees of the instrument.

To examine with accuracy the effect of different surfaces in radiating caloric, Mr Leslie painted one side of the vessel (a six inch cube,) with lamp-black, coated another with writing-paper, covered the third with a pane of glass, and left the fourth clean. The black side of the vessel thus prepared and filled with boiling water, being placed so as to front the reflector, the liquor in the thermometer rose 100 degrees of its scale. The papered side caused a rise of 98 degrees; the glass surface 90 degrees, and the clean metallic surface not more than 12°. These numbers, therefore, express the different powers of these surfaces in *radiating* caloric, as in all the experiments the quantity radiated was different, though the temperature of each surface must have been the same *.

Mr Leslie's next experiments shew the effect of different surfaces in *reflecting* radiant caloric. If the ball of the thermometer in the focus of the mirror be coated with tinfoil, the rise of temperature which it now suffers is much less; from the blackened surface it receives an increase of temperature, instead of 100°, amounting only to 20°, and from the metallic surface, instead of 12° only 2° ½; in other words, the ball thus covered with metal *reflects* the greater part of the calorific matter directed upon it, and therefore its temperature is not raised. The same thing is proved by substituting for the tinned mirror a glass one, (employing the thermometer in its usual state, or with-

* Leslie on Heat, p. 17.

out the tinfoil) : on presenting even the most powerful radiating surface, that is the blackened side of the cube, the rise of the thermometer will be merely a visible space, or the glass is capable of reflecting on the thermometer in its focus only a small part of the caloric it receives. If its surface is blackened, by spreading china-ink over it, even this slight effect ceases, or no rise in the thermometer is perceptible ; but if the surface of the glass mirror be covered with tinfoil, the effect on the thermometer is now increased to at least ten times the effect produced by the glass alone *.

We perceive, therefore, from these experiments, that the power of bodies to *radiate* caloric, and that to *reflect* it, are precisely opposed to each other. A blackened surface radiates most, glass next to it, and a polished metal least ; while in the power of reflecting, the order is precisely the reverse, the metal surface reflecting most copiously, the blackened surface least. It appears also, that the radiating and absorbing powers of bodies are exactly proportional, and are inversely as the reflecting power. Thus, a thermometer covered with metal is much less heated than when its glass surface merely is exposed, and we know that when the glass is blackened, the rise of temperature, which is indicated is still more considerable. That the power of reflecting should be inversely as that of absorbing, is to be expected, but it

* Leslie on Heat, p. 21.

could scarcely have been inferred *à priori* that the powers of radiating and of absorbing should be the same.

Mr Leslie found, that a considerable aberration takes place in the reflection of heat. He compared it with light, by placing a taper before the reflector, at the same distance with the canister, when he found, that on moving the taper aside, two inches from the axis of the reflector, no luminous spot could be perceived in the focus. But when the canister was moved in the same manner, it still continued to produce its heating effect on the thermometer in the focus; at the distance of an inch this did not appear to be lessened, and the canister could be withdrawn 7 or 8 inches from the axis before the effect ceased to be perceptible. It follows from this, that the heating effect will not be in the true focus, but nearer to the mirror. And accordingly, Mr Leslie found, that on advancing the thermometer half an inch nearer to the reflector than the focus, the heating effect was augmented more than one-third; and even at one inch, it was greater by one-fourth; while, on the contrary, in moving it backwards, the impression diminished rapidly, beyond the real focus; at half an inch beyond it, it was diminished one-half; and at one inch, did not amount to one-seventh of the effect. These facts are shewn by the following numbers: In the true focus, the thermometer, (the canister being placed before the reflector), stood at 58°; half an inch nearer to the reflector, it stood at 80°; one inch nearer, at 70°; half an inch

beyond the focus, on the other side, at 25°; and half an inch farther, at 8° *.

The next set of experiments which Mr Leslie made, and which are the last I shall have to state, are those from which he more particularly inferred the theory he has formed of Radiant Caloric. They relate to the effect of interposed skreens in intercepting the communication of temperature from the hot body to the mirror.

A frame being provided, larger than the reflector, a sheet of tinfoil is attached to it, and it is placed about two inches from the tin vessel, between it and the thermometer; the most powerful radiating surface of the vessel, the blackened one, being presented. The effect on the thermometer is completely intercepted, and will remain so at whatever distance the skreen is placed between the tin vessel and the reflector. Gold leaf, which is 600 times thinner than the tinfoil, has the same effect.

If, however, instead of the metallic skreen, a pane of glass be interposed, the result is very different; the liquor in the thermometer will be raised 20 degrees, estimating the entire and unobstructed effect from the blackened side of the cube at 100°. If, instead of the glass, a sheet of paper be attached to the frame placed between the heated tin vessel and the mirror about two inches from the former, the rise of the differential thermometer is rather greater, being 23 degrees when the blackened surface has been opposed to the mirror.

* Leslie on Heat, p. 61—64.

It might be supposed, that the effect produced on the thermometer in these experiments with the glass or paper is owing to part of the radiant caloric passing through their substance, while another portion is intercepted. But, were this the case, Mr Leslie observes, the effect ought to be the same, at whatever distance the skreen was placed between the tin vessel and the reflector, while he finds it to be entirely dependent on its contiguity to the former. If distant about two inches from the heated surface, the effects above stated are produced; if farther removed, that is, nearer to the reflector, the effect diminishes; and at length, when it is about a foot distant from the tin vessel, the rise in the thermometer is not one-thirtieth what it amounts to in the first position. This he regards as a proof that the interposed skreen does not operate partly by intercepting and partly allowing the radiant caloric to pass through it, but that the effect must be ascribed to the calorific influence being entirely arrested, while the skreen by this acquires heat, "and in its turn displays the same energy as if it had formed the surface of a new cannister of the corresponding temperature." Of course, the effect must be dependent on the contiguity of the interposed skreen to the source of heat, and on its nature with regard to its receptive and discharging powers; when, of metal, the effect is imperceptible, because a metallic surface is equally unfavourable to receiving caloric on the one side or giving it out on the other; while, if of glass or paper, the effect is considerable, because these substances are possessed of precisely the opposite powers; either of

them will receive the heat from the hot body, and at the other surface will give it out to the mirror.

In confirmation of this view, Mr Leslie found, that when a substance is used as the skreen which cannot have its temperature raised, as a thin sheet of ice, it completely intercepts the effect on the thermometer; and it is still farther established by an extremely ingenious experiment contrived by Mr Leslie, and which he justly regards as the *experimentum crucis*. Let two panes of crown glass be coated, one on each side with tinfoil; join them together with their tin surfaces in contact, and attach them to the frame placed in the same position as in the preceding experiments, the thermometer will experience a rise equal to 18 degrees. But let the panes of glass be joined, so as to have their tin coatings on the outer sides, there will be no rise whatever in the thermometer; yet, in both cases, the obstacle presented is the same; and if the effect on the thermometer were owing to radiant caloric being partly transmitted, it would be difficult to assign any cause for so striking a difference. On the principle already stated, it is fully explained. In the first variation of the experiment, a surface is presented to the tin vessel highly receptive of caloric, and therefore the compound skreen will be heated; and, on the other hand, a surface is at the same time opposed to the mirror, which will discharge as quickly the caloric it had received. In the other position, the circumstances are reversed; the metallic surface opposed to the tin vessel does not absorb the caloric projected towards it, but throws it off; and, on the

other hand, were it even heated, the metallic surface opposed to the mirror has equally little power of radiating; from both causes, therefore, the effect on the thermometer is imperceptible.

From the experiments now recited, Mr Leslie draws the conclusion, that the calorific emanation is incapable of permeating solid substances. He farther infers that it is not light; that it is no subtile fluid projected in right lines with velocity; but is merely the ambient air; and this is the theory he maintains with regard to the nature of radiant caloric. He conceives that heated bodies communicate to the air immediately in contact with their surface, part of their high temperature; this heated air suffers expansion, and a pulsation, or undulation is successively propagated from the heated surface in an extended chain. The expansions, he observes, of aëriform fluids are very considerable, the particles of air which come into contact with the heated surface are therefore forced to recede, and they acquire, in the space of receding, an impetus which thence displays itself in a continual progressive or vibratory motion, which is carried forward, collected in the mirror, reflected, and condensed in its focus. "The mass of air without sensibly changing its place, suffers only a slight fluctuation as it successively feels the partial swell, but the heat attached to this state of dilatation is actually transported, and with the swiftness of sound."

On this hypothesis Mr Leslie explains the principal facts with regard to radiant caloric. It is obvious that the higher the temperature of the surface is from which the chain of pulsations commences, the more must the

atmospheric air be heated, the expansion will be greater, or will be more rapidly renewed, and hence the calorific emanation will appear to be greater. But different kinds of surface at the same temperature radiate apparently very different quantities of caloric, a difference which Mr Leslie supposes to arise from the more or less perfect contact of atmospheric air with these surfaces; those with which the air will come into closest contact, will of course communicate to it the largest quantity of caloric, or will communicate it most rapidly; and from them, therefore, the calorific emanation at a given temperature will appear to be greatest. For the same reason, such surfaces will be those which absorb most readily what is termed radiant caloric, or which, in experiments like the preceding, will be most heated. And, lastly, on the same hypothesis, the effect of skreens interposed between the hot body and the mirror is explained; they will always arrest a part of the calorific radiation by intercepting the chain of pulsation, while at the same time being capable, to a certain extent, of putting the atmospheric air into such a state, they will propagate it in part, and those which will do so to the greatest extent will be those which are beft adapted to excite originally such undulations; a conclusion which ſtrictly accords with the fact.

With regard to this hypothesis, I must observe, that though it may be assumed, and seems adequate to explain the phenomena, it does not appear to follow necessarily, as Mr Leslie has presumed that it does, from the particular phenomena from which it is inferred. The phenomena are those which relate to the effect of

interposed skreens, which he regards as explicable only on the hypothesis of the air being the vehicle of the communication of heat. But in drawing this conclusion, he assumes that by those who maintain the existence of radiant caloric as a distinct matter, the effect of these skreens must be explained, on the supposition that they allow part of the radiant caloric to pass through, while they arrest the rest, an hypothesis which, it has already been observed, does not accord with the facts. It is by no means necessary, however, that this hypothesis should be assumed, or that it should be supposed, admitting the existence of rays of caloric, that they must be capable of penetrating in part transparent bodies, and that to this the effect of the interposed skreens must be ascribed. On the contrary, the phenomena may be accounted for on the principles already stated,—that the substance of the skreen at one surface intercepts the whole of the calorific rays; that by this its temperature is raised, and it then begins to radiate caloric from the other, in quantity proportioned to the power of the interposed substance of absorbing and emitting caloric. In truth, the explanation must on either hypothesis be the same. The effect on the thermometer, when a skreen is interposed, must be ascribed to the interposed substance receiving caloric at the one surface, and discharging it at the other; and this, whether the caloric conveyed to it on the one side, or discharged from it on the other, be supposed to be propagated by pulsations in the atmosphere, or by actual projection of calorific particles. And on either hypothesis, those substances which are best disposed to receive on the one hand, and give it out on the

other such as glass or paper, will be those which will admit of the greatest effect being still produced on the thermometer, while those which are worst adapted to receive or to radiate caloric, as metals, will be those least capable of propagating either the pulsation, or the calorific emanation.

Nor, I confess, does it appear to me, that the phenomena are even explained on the hypothesis that the air is the medium of communication. How is the velocity of communication to be accounted for? It is admitted by Mr Leslie, that it cannot be supposed, that a succession of heated particles of air moves from the hot body, or that the particles heated at its surface are darted forward, and impinge on the body the temperature of which is raised. Such a supposition, he admits, is "incompatible with the laws of fluids, and directly refuted by experiment." Neither does it appear to be imagined, what is indeed equally liable to objection, that by a chain of undulations, the portion of air heated and expanded at the hot surface, will change its place, be moved forwards, reach the thermometer, and be succeeded by a new wave of heated air, which shall observe the same motion. It is supposed, therefore, that by the heated body, the air is thrown into oscillations or undulations; that these continually renewed at its surface, are propagated in a right line, and that at each undulation, the caloric is discharged, so as to be conveyed forward with the same velocity *. But while it is admitted,

* Experimental Inquiry, p. 242.

that such undulations might be excited, by what agency is this transfer of caloric effected? Suppose a layer of air to receive heat from the hot body, and to be expanded, from this expansion it may press on the contiguous layer; but does it follow, that while it impresses this motion, it shall, at the same time, discharge the heat it had received? There is no connection between these effects, nor is there any thing in the propagation of this undulation, that can cause or accelerate the discharge of caloric, which should actually be propagated with as much celerity through the air at rest, if this condition could be obtained, as in air subjected to these pulsatory waves; and as we know that caloric is transmitted slowly through aëriform fluids, especially in a horizontal direction, the phenomena of radiant caloric cannot be explained on such an hypothesis.

I may add, that Mr Leslie's explanation is quite incompatible with the facts established by the experiments of Herschel and Englefield, as to the existence of a calorific matter in the solar rays. These prove the existence of radiant caloric as a distinct subtle matter, capable of rapid projectile motion, and until invalidated by experiment, must be regarded as affording proof of the truth of the common opinion.

The last experiments on this subject of which I have to take notice, are those by Count Rumford, published subsequent to Mr Leslie's, and, so far as they extend, extremely similar to them; so much so, indeed, that it is unnecessary to do more than state their results. A clean polished metallic surface, he

found to radiate much less caloric than a metallic surface at the same temperature blackened. The different metals, when at the same temperature, according to his experiments, have the same power of radiating caloric; which, however, does not accord with the experiments of Mr Leslie. Animal substances, such as membrane, he describes as throwing off much more calorific matter by radiation, not less than 25 times more, than a polished metallic surface at the same temperature. And he adds the general remark, that the comparative powers of these substances are the same in absorbing as in radiating caloric *.

Count Rumford, not admitting the existence of caloric as a distinct matter, endeavours to explain the phenomena of radiant caloric from the hypothesis of undulations excited by bodies at high temperatures in an etherial medium.

Besides the theories of radiant caloric which I have already stated, I may, in concluding its history, take notice, though very briefly, of the hypothesis with regard to its nature, which was advanced by Dr Hutton. Conceiving it to be an unphilosophical assumption, that caloric should be capable of radiation, he endeavoured to shew, that light is the agent concerned in the production of these phenomena. Assuming, that the heating power of the different species of visible light, is not proportioned to their power of exciting vision, he conceived that there might be a spe-

* Philosophical Transactions for 1804, p. 109. 112. 119. 128.

cies of light capable of exciting temperature, but incapable of producing illumination. And what has been termed Radiant Caloric, Dr Hutton supposed may be light of this kind.

The objection to the common theory of radiant caloric, from which this hypothesis has been deduced,—that caloric cannot be supposed capable of radiation, and that the property of moving in right lines, with great velocity, must belong to some species of light, is a mere assumption, in support of which no evidence is attempted to be brought. Considering caloric with the generality of modern chemists, as a subtle matter, *sui generis*, there is no incongruity in the supposition, that its particles may be projected from bodies, and that these, in moving, may obey similar laws to those of light; nor does it at all follow, that light should be the only matter susceptible of this projectile motion.

In their properties they are altogether dissimilar, at least so much so, that we must regard them as distinct kinds of matter. The calorific rays are incapable of exciting vision; nor is this owing merely to their tenuity, since, when concentrated by a mirror, they do not produce any sensible illumination. While light passes with facility through rare media, through transparent fluids, and through glass, radiant caloric does not pass through fluids, is in a great measure arrested by glass, and according to the experiments of Pictet, is retarded in its motion even by the atmospheric air. Nor can we trace any intimate connection between them in their chemical properties. Light ex-

erts certain chemical agencies by which it is characterized as a peculiar kind of matter. Now these properties are not possessed by radiant caloric; nay, what at once shews the opposition between them, the peculiar agencies of light are exerted with most effect, as I shall afterwards have to state, by those rays which have the least heating power, the indigo and the violet; while, by those which are most powerful in exciting heat—the red rays, the chemical effects are produced in the weakest degree; and radiant caloric, unconnected with light, is entirely destitute of these peculiar chemical powers, as I have found by experiment. If a distinction is to be established between two bodies, it must be drawn chiefly from a comparison of their chemical properties, and if these differ, they must be regarded as distinct kinds of matter.

Lastly, The very foundation of Dr Hutton's hypothesis is overturned; for it may be justly questioned, whether any of the species of light have the power of exciting heat. From the experiments of Herschel, already stated, it appears, that the heating power of the solar rays is owing to the radiant caloric they contain, and which is separable from the visible light with which it is associated. When a solar ray is decomposed by a prism, the less refrangible calorific rays are separated from the rays of light which are more refrangible, and the more complete the separation is, the less heating power is discoverable in that part of the spectrum which the visible rays occupy; and were the whole rays of caloric withdrawn, we have no reason to believe, that the visible rays of light would excite any

heat. The hypothesis of Dr Hutton, therefore, must be relinquished, since the phenomena of radiant caloric cannot be explained on the supposition that it is a species of light, if light itself, apart from this matter, has actually no heating power.

At the same time, there is a very strict connection between light and radiant caloric; and we have seen, too, that there is even a gradation in the properties of radiant caloric, connected with its association with light, as is very distinctly shewn by the fact, that the calorific rays projected from heated bodies, are nearly incapable of penetrating glass, while those existing in the solar beam are transmitted through it with little impediment; and that these rays differ in the order of their refrangibility, those being most refrangible which have least heating power. The hypothesis is perhaps not an improbable one, that radiant caloric may be composed of light and caloric,—that this combination may take place in different proportions, giving rise to rays of different powers, and may extend even to the different rays of visible light.

From the various experiments I have now stated, it appears, that caloric is diffused over matter in two modes. One part of it is thrown from the surface of bodies, in right lines, with the greatest velocity, while another part is more slowly diffused, by communication from particle to particle, until an equilibrium of temperature is established.

It would be interesting to discover what is the re-

lation between these two powers. By comparing the experiments on the radiating powers of bodies, with those on their conducting powers, it appears to me that the proposition that they are inversely as each other, is nearly just. Thus the metals are the best conductors, but they are least powerful in radiating; glass radiates powerfully, while it conducts very imperfectly. A spongy covering diminishes much the conducting power, while it augments greatly the radiation. Nor is there merely this general coincidence with the law I have stated; we farther find it confirmed in more minute differences. According to Mr Leslie's experiments, the radiating power of lead being as 19°, that of iron is 15°, and of tin 12° *; but, according to the experiments of Ingenhouz, already quoted, and which, in determining this question, are to be preferred to Richman's as the conducting was ascertained apart from the radiating power, lead is the worst conductor, iron is superior to it, and tin again is superior to iron. Hence, in the general point of view under which such experiments ought to be taken, it appears to follow that the radiating is inversely as the conducting power.

It is difficult to discover what proportion the caloric discharged by radiation from a body suffering reduction of temperature, bears to that which it gives out by slow communication, or in which of these modes the largest quantity of caloric is discharged.

* Inquiry, p. 78, 79.

On this interesting subject, some experiments have been made by Mr Leslie, and with some similar ones by Count Rumford, afford us the only information we have with regard to it.

That the slow communication of caloric to the surrounding medium, has an important share in the cooling of bodies, is evident from the familiar fact that the celerity of cooling is different, according to the nature of that medium; and in particular is greater or less, according as the matter in contact with it is a better or worse conductor of caloric. Suppose a thermometer at a high temperature is suspended in the Torricellian vacuum, it will begin to cool, and will continue to do so until it arrive at the temperature of the external atmosphere. The time of its cooling, as ascertained by Count Rumford, from 212° to 32° of Fahrenheit, will be 10′ 5″. If it be surrounded with atmospheric air, the time of its cooling the same extent will be only 7′ 3″; if surrounded with water, 1′ 5″; and if with quicksilver, not more than 0′ 36″ *. And in these cases it will also be found that the different substances have suffered different augmentations of temperature, and that they have therefore influenced the cooling by their different conducting powers. Here, therefore, it is obvious that the surrounding matter, though it might impede the radiation, has on the whole accelerated the cooling.

The same fact is demonstrated by the effect of a current of air in accelerating refrigeration, and which

* Rumford's Essays, vol. ii. p. 425.

is independent of any influence on radiation. Mr Leslie exposed two tin globes, filled with warm water, the surface of one being painted with lamp-black, that of the other being clean, to air in different states of motion. When exposed to a gentle breeze, the clean globe lost half its heat in 44 minutes, the painted one half its heat in 35′. When exposed to a strong breeze, the times were 23′ and $20\frac{1}{4}'$, and to a vehement breeze only $9\frac{1}{2}'$ and 9′*. Here we perceive clearly the influence of the conducting power on the refrigeration. The atmospheric current could not accelerate the radiation, but it would materially the slow abstraction, by removing more quickly the heated air, and applying a fresh portion at a lower temperature. And it appears that its effect on both surfaces was nearly or precisely the same, since in proportion as the current or change of atmosphere was rendered more rapid, and of course predominant over the other cooling causes, the rate of cooling in the globes approached more to equality.

The effect of the radiation from a hot body on its cooling, has been ascertained by Mr Leslie, by some very excellent experiments made by cooling water in vessels, the surfaces of which radiated unequally, and observing the effect on their times of cooling.

A hollow globe of tin filled with warm water, and having a thermometer inserted in it, was exposed to the air of a room, and its progress in cooling observed. It sunk from 35° to 25° of the centigrade scale, in

* Inquiry, p. 271.

156 minutes. It was then coated with lamp-black, and on repeating the experiment, the time requisite for the same extent of cooling was only 81 minutes *.

From this experiment, and knowing the law of the cooling of bodies, it was easy to deduce the time in which the vessel would have spent its whole charge of heat, if it had continued to suffer the same uniform diminution as at first. With the metallic surface the limit would be 225 minutes, with the painted surface 117; in other words, the former must have lost every minute the 225th part of its heat, and the latter the 117th part. But we know, that if the heat were abstracted by radiation only, the metallic surface ought to cool eight times slower than the painted one, or expend only the 936th part of its charge of heat each minute. Its actual rate of cooling from the experiment, is found to be more than 4 times greater than this; hence it follows, that this difference must have arisen from the discharge of its caloric, to the surrounding medium, by slow communication. The experiment is a striking one, as it shews the superiority of radiation to slow evolution in reducing temperature, since even when the globe was covered with a substance which is no doubt a bad conductor, instead of cooling more slowly, it cooled faster, from this covering promoting radiation.

It is to be observed, however, that this proportion will not be the same at all temperatures, and it is necessary to attend to a circumstance by which it is alter-

* Inquiry, p. 268.

ed. The cooling of a body in atmospheric air, is accelerated by the current formed in the atmosphere in contact with it, from the expansion it suffers by its temperature being raised. Now, at high temperatures, the contiguous air being more quickly heated than at lower temperatures, this current ascending from the heated body, will be more rapid, and will, therefore, have a greater effect in reducing its temperature. Accordingly, by repeating the experiment at a higher temperature, (80 degrees above that of the surrounding atmosphere), Mr Leslie found the proportion different: the respective rates of cooling of the clean and the painted ball, which, by the former experiment, were as 13° to 25°, were now as 13° to 19°; and from the two he established the general result, "that at low "temperatures the portion of heat dissipated from a "painted surface, by the repetition of aërial contact, "is somewhat less, and in high temperatures consider-"ably greater than what is spent by radiation *."

Similar differences are found to exist, when experiments are made on a clean metallic vessel, and on the same vessel coated with isinglass or covered with paper, or on a thermometer, with its bulb uncovered, and covered with gilding; and from these also, similar conclusions are deduced. And, lastly, the general effect of radiation in cooling bodies, though not its precise extent, is shewn by the striking fact, that the peculiar nature of the surface has no effect on the celerity of cooling, when the body is immersed in water; the

* Inquiry, p. 276.

clean and the painted globe for example, it was ascertained by Mr Leslie, losing their heat in water with exactly the same facility *. The reason is, that the radiation of caloric does not take place, when the body is immersed in a fluid, and hence its cooling must be effected entirely by the slow evolution of caloric, and must be dependent partly on the conducting power of the fluid, and partly on its expansibility and mobility, by which its internal motions will be accelerated.

These observations on the effect of these circumstances in accelerating refrigeration, open a field of investigation which may be of much importance in practical chemistry, and some singular facts with regard to it have been discovered by Mr Leslie, particularly on the times of cooling in vessels, the surfaces of which are variously altered †.

A tin vessel filled with boiling water, suffered a reduction of temperature from 60 to 30 degrees of the centigrade scale in 81 minutes. When the sides were rubbed with quicksilver, it made the same descent in 78′. The clean instrument sunk from 30° to 15° above the temperature of the air of the room in 108′; when rubbed over with oil in 87′; and when covered with bibulous paper soaked in oil in 58′. The metallic vessel filled with warm water sunk from 20° to 10° above the temperature of the room in 117′; when covered with a pellicle of isinglass, it cooled much more quickly, and that with a celerity proportioned to the thick

* Inquiry, p. 316, 317.

† Ibid. p. 333.

ness of the pellicle. With one calculated to be the 50.000th of an inch thick, it sunk to the same extent in 101′, with one the 10.000th in 82′, with one equal to the 1.000th in 63′, and with one equal to the 300th in 61′. These results are striking, since the coverings given to the surfaces must have impaired the conducting faculty, but this was more than compensated for, by the increase they gave of radiating power. At the same time there can be no doubt, but that if these additional coverings be made too thick, they may counterbalance the increased radiation, by acting as an imperfect conducting medium. This is very evident in an experiment of Pictet, in which the bulb of a thermometer, blackened by being held over the flame of a candle, was more quickly heated than when clean, yet, at the same time, instead of likewise cooling faster, it cooled more slowly, in the proportion of 5 to 6, the thickness of the covering no doubt impeding the discharge by communication, more than that by radiation was augmented.

Count Rumford has made some similar observations. Thus a metallic cylindrical vessel, with its sides bright, and filled with warm water, requiring 55 minutes to cool a certain extent of the thermometrical scale, a similar vessel, when its sides were covered with linen, cooled to the same extent in $36\frac{1}{2}$ minutes; when covered with a coating of glue, it cooled in $43\frac{1}{4}$ minutes, and when an additional coating was put upon it, in $37\frac{5}{8}$. Varnishing the surfaces had the same effect, the maximum being at 4 coatings, when it cooled in

30¼ minutes. A covering of lamp-black caused it to cool in 34 *.

A conclusion somewhat singular appears to be established by some of Count Rumford's experiments, that water in vessels of different metals cools with precisely the same celerity. His standard vessel was of brass; and repeating the experiment with it covered with gold and silver leaf, and likewise in similar vessels of lead and tinned iron, the times of cooling were in all of them precisely the same †. We have seen, that the conducting power of the substance has always a certain effect on the cooling; and in this power these metals differ considerably. We might expect, therefore, that, from this cause, the times of cooling in these experiments would be different. It appears, too, from Mr Leslie's experiments, that the metals differ even in their radiating power, as has been already stated; and by this also the results must be varied. Perhaps, however, these experiments throw light on each other. We have seen reason already to conclude, that the radiating is inversely as the conducting power, and they may therefore counterbalance each other; and thus, in vessels of different metals, the times of cooling may be nearly or altogether the same. The assertion, however, that the different metallic vessels allow water to cool with the same celerity, is inconsistent, I must remark, with the experiments of Richman already quoted, on the celerity with which

* Philosoph. Trans. for 1804, p. 90, &c.

† Ibid, p. 111.

the thermometer cools, when its ball is encased in globes of the different metals.

The applications of these facts, as suggesting the means of accelerating refrigeration, are abundantly obvious. Some have been particularly pointed out by Count Rumford. Polished metallic surfaces being those which radiate the least quantity of caloric, in cases where it is wished to prevent a fluid from cooling quickly, the end will be better attained by confining it in a metallic vessel, the surface of which is bright, than if it were covered with any matter, as, on the supposition of impairing its conducting power, we might be led to do. On the other hand, if our object be to cool the liquor as speedily as possible, the external surface of the vessel should be painted or blackened. Metallic tubes, for conveying or confining steam, without condensing it, as those used in the steam engine, should be kept clean and bright on their external surface, while, if our object is to condense the steam as quickly as possible, as in heating rooms by it, they ought to be painted or covered with any substance which radiates caloric abundantly *.

WITHOUT separating the effects of the various modes in which the temperature of a body is reduced, it is of importance to know the law it observes, and accordingly this subject—the actual rate of cooling of a body in any medium, has been repeatedly the

* Philosoph. Trans. for 1804, p. 177.

subject of investigation. It is obvious, from what has been already stated, that different bodies will cool with different degrees of celerity, when placed even in the same medium; and likewise, that the same body will cool with different celerities in different media. But, independent of such comparative differences, what is the rate of cooling in any body, in any medium, or what is the law it observes in giving off its caloric?

It could not escape observation, that the greater the difference between the temperature of a hot body, and that of the surrounding medium, the more caloric does it give out in a certain time, and that it communicates less, or cools more slowly, the nearer its temperature approaches to that of the matter around it. But by what proportion is this regulated?

Newton seems first to have investigated this subject *. From observing the rate of cooling in a mass of iron, which had been raised to a red heat and exposed to the atmosphere, and marking the changes of temperature it suffered in certain times, he concluded, that the quantities of heat lost by a body in small portions of time, are always proportional to the excess of heat subsisting in it, or to the excess of its temperature above that of the surrounding medium. Hence, taking the times in arithmetical progression, the decrements of temperature will be in geometrical progression; and the heats remaining, considered as the differences between the temperature of the body and of the surrounding medium, will observe the same law. This

* Philosoph. Trans. abridged, vol. iv. p. 3.

law has been generalized, and applied equally to the heating of a body, by Richman, in consequence of his own numerous experiments, and those of Kraft, and expressed in the following terms: In the heating or cooling of a body exposed to a medium, of which the temperature is constant, the times being in arithmetical progression, the differences between its temperature and that of the medium are in geometrical progression *.

According to this law, therefore, if a body preserving its form be supposed to have an excess of temperature above the surrounding medium equal to 10 degrees, in cooling, suppose that the first minute it loses one degree, the reduction the second minute will still bear the same proportion to the remaining excess; or considering this now as 10°, it will be $\frac{1}{10}$; and thus proceeding, we find, that each time the 10th part of what remains being evolved, the heat given out must be uniformly diminishing, because the excess itself, of which it is a constant part, is always becoming less.

Experiments appear to agree in general with this law. If it be strictly true, however, one singular corollary flows from it, that no two bodies, once unequally heated, can ever arrive at an equality of temperature; or no body heated above the temperature of the surrounding medium, can ever truely arrive at the temperature of that medium. From considering this, Mar-

* *Novi Comment. Acad. Petropolit.* t. i. p. 174.

tine inferred, " that the decrements of heat are partly equable, and partly in proportion to the subsisting heats ;" so that in the cooling of a body, taking the times in arithmetical progression, the decrements will consist of two series ; in the more important one they will be in proportion to the heats themselves, or in geometrical progression ; in the other, and subordinate one, they are equable, or equal quantities of heat will be lost in equal times * ; a correction which, while it obviates the above difficulty, makes little difference in the practical application of the law to ascertaining very high temperatures.

Either expression of the law, however, is just only while the condition holds of the temperature of the medium being constant. In the actual cooling of a body, variations will arise as to its uniformity, from the succession of currents in the surrounding medium, especially when that is an elastic, and therefore highly expansible one. The successive application of the surrounding matter always accelerates the cooling ; and this being more heated, or more caloric being communicated to it the first moments of cooling than afterwards, it will be more expanded ; the current will thus be more rapid at high than at low temperatures, and its effect, as an auxiliary in reducing temperature, will therefore be greater in the first periods of the body cooling than in the last. It is also evident, that if the motion of the medium is in the least degree confined, as its temperature will then increase as it re-

* Essay on the Heating and Cooling of Bodies.

ceives caloric from the hot body, the cooling of the latter will be no longer in this equable proportion.

In concluding the consideration of this part of the history of caloric, it is necessary for me to take notice of a very singular experiment, that of the apparent radiation of cold.

This phenomenon was first observed by the Florentine Academicians, though they seem to have been unwilling to admit its reality. They describe their experiment in the following manner: "We were desirous to try whether a concave speculum, exposed to a mass of ice weighing 500 pounds, would reflect any sensible degree of cold on a very delicate thermometer of 400 degrees, placed in its focus. The result was, that the thermometer instantly sunk: but a doubt remained, whether the thermometer was acted on more by the direct cold of the ice, or that reflected by the speculum. This doubt was removed by covering the speculum; and certain it is, (whatsoever might be the cause), that the spirit instantly began to rise again. Yet still we will not presume positively to affirm, that this rise might not have been owing to some other cause than the taking off the reflection from the speculum, all the precautions not having been taken which might be considered necessary to secure absolute assent to the experiment *."

* Nicholson's Journal, vol. x. p. 2.

Pictet, after having ascertained the radiation of caloric from a hot body, with the apparatus already described, placed in the focus of one of the mirrors he employed, a matrass filled with snow, and in that of the other, at the distance of 10½ feet, an air thermometer. The thermometer instantly fell several degrees of its scale, indicating diminution of temperature; and on removing the matrass, it immediately rose. On rendering the cold more intense, by pouring nitrous acid on the snow, the thermometer sunk five or six degrees more *. In this experiment, then, we have apparently displayed the radiation of cold.

The subject has been since prosecuted particularly by Mr Leslie, and likewise by Count Rumford; and this radiant cold has been found to observe, in its relations to different bodies, the same laws as radiant caloric. Like it, it differs in intensity according to the nature of the surface emitting it; and the difference is of precisely the same nature. The cubical tin vessel employed in Mr Leslie's experiments, being filled with ice, and opposed to the thermometer in the focus of the mirror, the reduction of temperature was found to be least from the metallic surface, greater from the glass surface, and still greater when the surface opposed had been blackened. The effect varies, too, according as the surface of the thermometer is altered; when it is gilt, the diminution of temperature is very inconsiderable, while, when it is blackened, it is still greater

* *Essais de Physique*, p. 82.

than when the clean glass surface is opposed. Lastly, the nature of the reflecting surface gives rise to similar variations as in the radiation of caloric. The effect is greatest from the clean metallic surface, less when the mirror is of glass, and still less when its surface has been covered with lamp-black. The powers of these surfaces, therefore, in radiating cold, in absorbing it, and in reflecting it, are precisely the same as their powers of radiating, absorbing and reflecting heat. Those which radiate it best also absorb it most readily, while these two qualities are opposed to ther eflecting power.

The effects arising from interposed skreens, Mr Leslie found to be also perfectly alike. If a sheet of tinfoil be interposed, the action of the cold body on the thermometer is intercepted; by a plate of glass, or a sheet of paper, it is only diminished, more or less so, according to the distance from the cold substance; and the effect of blackened or compound skreens is precisely the same as has been already stated, in considering the phenomena of radiant caloric.

In these experiments, then, we have apparently the emanation from a cold body of some positively frigorific matter, which moves in right lines, is capable of being intercepted, reflected and condensed, and of producing, in its condensed state, its accumulated cooling power; and they appear equally conclusive in establishing the existence of radiant cold, as the other experiments in establishing the existence of radiant heat.

The hypothesis, however, of a frigorific principle, has been banished from modern philosophy, since there

was no proof of its existence, at least prior to the present experiments; and since the phenomena, with the exception of those which they present to us, are explained with more simplicity, and in a manner more satisfactory and philosophical, merely from the abstraction of caloric.

In conformity, therefore, to the doctrine, that cold is simply the negation of heat, the necessity must be felt of giving an explanation of the phenomena established by these experiments, which shall accord with that doctrine, and not involve the supposition of the operation of a positive frigorific principle. Two such explanations have been advanced; one sketched by Pictet, the other by Prevost. In both, caloric is supposed to escape by radiation from the bulb of the thermometer, and to this the diminution of temperature which is produced is ascribed.

According to Pictet's view, this radiation is owing to the equilibrium of tension in the calorific fluid being broken by the introduction of the cold body. He supposes, that when a number of bodies in the neighbourhood of each other are in an equilibrium of temperature, there is no radiation of caloric among them; because, throughout the whole, the caloric exists in this equality of tension or elasticity, and a resistance is every where opposed to its radiating from any particular point. But, as soon as a body at a lower temperature is introduced, the balance of tension is destroyed, and caloric begins to radiate from all of them, until its temperature is raised to an equality with theirs. In the above experiment, therefore, in

placing before the mirror a cold body, as the cubical vessel with ice, it causes a radiation of caloric from the surface of the mirror, and this again, by a similar operation, causes a radiation from the thermometer in its focus, and hence the observed diminution of temperature *. In Pictet's words, the experiment made with the cold body differs in nothing from that with the hot one, but in the direction in which the calorific emanation moves. In the one, that, for example, where the heated ball is employed, it proceeds from the ball by the medium of the mirror to the thermometer; and in the other, the experiment with the ice, it moves in the opposite direction from the thermometer by the same medium to the vessel in which the ice is contained, the thermometer being now to the ice what in the other experiment the ball is to the thermometer †.

The view which Prevost gives is somewhat different. The principle on which it rests is, that caloric is radiated from all bodies at all temperatures, the quantity radiated being greater in proportion as the temperature is high. When a body is placed before the mirror whose temperature is superior to that of the thermometer in its focus, though the ball of the

* I have given this explanation as applying to the experiments made with the single mirror, as less complicated than with the apparatus with the two mirrors. The latter, however, will be sufficiently obvious, the reflection being merely repeated at the surface of each mirror.

† *Essais de Physique*, p. 85.

thermometer is radiating caloric, yet the hot body opposed to it giving out at the same time more caloric in the same mode; and this being reflected on it by the mirror, its temperature must rise. When both the substance made the subject of experiment and the thermometer are at the same temperature, neither suffers any change, because the quantity emitted from each being the same, and the reflection and condensation by the mirror being alike, each receives as much as it gives out. But when the temperature of the body placed before the mirror is inferior to that of the thermometer in the focus, though it is still radiating caloric, the quantity is inferior to what the thermometer radiates, the latter therefore receives less than it gives, and of course its temperature must fall *. Dr Hutton gives a similar explanation, substituting only the term invisible light for that of heat.

Either of these hypotheses appears at first view to afford a satisfactory explanation of the general phenomena of radiant cold. But when applied to the more particular phenomena, especially to the operation of different surfaces in increasing or diminishing the effect, they will be found perhaps in some points defective. Of the two, Pictet's is superior to that given by Prevost. Mr Leslie, too, has very happily applied his theory of aërial pulsations to this subject; the cold surface abstracts part of the caloric of the contiguous layer of air, whence a momentary contraction of that layer follows, and pulsations accompanied with a discharge

* *Recherches sur la Chaleur*, p. 15.

of heat to the cold surface, and consequently, from the mirror and the thermometer, are established, observing the same laws, as he supposes, as in the case f radiant heat.

But should even the phenomena not be satisfactorily explained, this can scarcely lead to the admission of the agency of a positively frigorific power. The various facts connected with temperature are so well explained by the operation of caloric alone, that we must feel reluctant to admit the introduction of an antagonist power. Increase of temperature, with all its consequences, expansion, fluidity, and vaporization, are satisfactorily accounted for by the introduction of caloric in various quantities, and diminution of temperature of course by its abstraction. And we should merely render the explanation embarrassed, and not more satisfactory, if we should suppose the existence of a frigorific power, which enters bodies when caloric is withdrawn, and which is expelled when it is communicated.

Sect. IV. *Of the Comparative Quantities of Caloric which Bodies contain.*

In homogeneous bodies, the quantities of caloric which they contain are proportioned to their temperatures and quantities of matter. It is found to be so on experiment, and that it should is nearly evident, *à priori*; for the particles of different portions of the same matter being alike, their powers must be equal,

and no cause can be imagined why one portion should have a relation to caloric different from the other, or require a different quantity to raise its temperature.

Since caloric is the cause of temperature, and since, in each body, the increase or diminution of temperature is proportioned to the addition or abstraction of this power, it might be supposed, perhaps, that, with regard to heterogeneous bodies, the same law would be observed, and that in equal quantities, and at the same temperature, the same quantity of caloric would be contained in each.

On making the experiment, however, this is not found to be the case. If a number of bodies of different kinds, water, oil, mercury, and others, in equal weights, and at the same temperature, be exposed to a common source of caloric, they all receive it; their temperature will rise with different celerities; but in a certain time they will all have arrived at a common temperature. It will be found, however, that in arriving at this temperature they have absorbed very different quantities of caloric; the water will have taken in more than the oil, and the oil more than the mercury. Now, it is evident, that although we suppose that at the commencement of the experiment these substances contained equal quantities of caloric; yet, at the temperature to which they are all raised, they must contain unequal quantities, since, in suffering this rise, each absorbed a quantity different from the others. But, in like manner, it might be shewn, by beginning the experiment at a still lower temperature, that, at the temperature from which they were

raised, the quantities of caloric they contain must have been unequal; and as the same cause that disposes one body to absorb more caloric than another must be something peculiar to it, and of course must always continue to operate, it follows, that at every point in the scale of heat, different bodies contain very different quantities of caloric when in the same weights and at the same temperature.

The same truth is established by communicating equal measured quantities of caloric to different bodies, when we find that their temperatures are not equally raised, but that the quantity which raises one body one degree will raise another 20 or 30 degrees.

Boerhaave began the investigation by which this law was established. Observing that dense bodies were those which abstracted heat most rapidly, from a body at a superior temperature, he imagined this might be owing to the denser mass having a disposition to contain more of this power than the other. To ascertain this, Fahrenheit, at his desire, made the experiment, which, although Boerhaave failed in drawing the proper conclusion from it, is the basis of the discovery. It consisted in first mixing together equal quantities of the same fluid,—as alkohol, or water, or oil, at different temperatures. Of course, the mixture immediately attained a common temperature; and this was found by the thermometer to be, as Boerhaave reports it, half the excess of the hotter above the colder; or, if 1 lb. of water at 212° were mixed with 1 lb. at 32°, the former lost 90° of its temperature, which were communicated to the other.

Here, therefore, the distribution was regulated by the quantity of matter. But when equal quantities of two different bodies,—of water and quicksilver, at different temperatures, were mixed together, the result was different. If the water were hotter than the mercury, when equal bulks of them were mixed together, the temperature of the mixture was greater than the half; and, on the other hand, if the quicksilver were hotter than the water, still mixing equal volumes of them, the resulting temperature was always less than the half of the difference. When three parts of mercury by volume were mixed with two of water, at different temperatures, the temperature produced corresponded always to half the difference of the temperature in each, or was the mean between the respective temperatures, the same as when equal quantities of water were mixed together *.

From this experiment, Boerhaave inferred justly that caloric is not distributed in bodies according to their density or quantity of matter. If it were, it is obvious that as quicksilver is 13 times heavier than water, the addition of a quantity of mercury at a higher temperature than that of the water with which it is mixed, ought to have an effect in raising the temperature of that water equal to what the addition of 13 times the bulk of water at that temperature would have; while the experiment shews, that the effect of the mercury in raising the temperature of the water, is not equal to the effect which even one measure of

* *Elementa Chemiæ Boerhaav.*, t. i. p. 269.

water, at the same temperature with that of the mercury, would have.

It is singular, however, that Boerhaave should have drawn a conclusion equally inconsistent with the experiment,—that caloric is distributed in bodies according to their volumes, or the spaces they occupy; since it is evident, that were this the law, the temperature resulting from the mixture of equal bulks of water and quicksilver ought to have been the arithmetical mean, and it would not have been necessary to produce this mean to take three of mercury to two of water.

Dr Black appears to have been the first who perceived the error of Boerhaave,—who estimated sufficiently the value of the experiment; and who drew from it the just conclusion, that the quantities of caloric which heterogeneous bodies contain at the same temperature, are proportioned neither to their weights nor volumes, but are distributed in proportions regulated by the force of that attraction which they have for this principle *. The experiments which this view suggested, were made previous to the year 1765; and so early as 1760, Dr Black had perceived the general fact with regard to the distribution of caloric.

Wilcke, in 1771, read a dissertation before the Academy of Sciences at Stockholm, afterwards published in their memoirs, in which he announces the same principle, as established by his own experiments; and his

* Black's Lectures on Chemistry, vol. i. p. 79. and 504.

method of determining the relative quantities of caloric which bodies contain is somewhat different, as I shall immediately have to remark, from that first employed by Boerhaave. Dr Irvine of Glasgow, and Dr Crawford, acquainted with Dr Black's discovery, prosecuted the subject, and subjected many substances to experiment. Some additions were also made by Lavoisier and Gadolin; and, by the labours of these different philosophers, the general law has been established,—*that different bodies in equal quantities, whether estimated by weight or volume, contain at any given temperature unequal quantities of caloric.*

That this is the case, is sufficiently evident from the experiment of Boerhaave, already stated. It is equally obvious from many other examples. Thus, if we subject to experiment equal *weights* of water, of glass, of tin, of copper, of silver, and of lead, we find that these equal weights, instead of containing at the same temperature equal quantities of caloric, contain very unequal quantities. If the water contain 1000°, the glass, on experiment, will be found to contain not more than 187°, the copper 114°, the silver 82°, the tin 60°, and the lead 42°; or these respective quantities of caloric communicated to these substances, will produce the same rise in their temperatures. If, again, we take equal *volumes* of them, we still find their caloric not proportioned to these. If a given volume of water contain 1000 parts, the same volume of glass will contain only 448 parts, the copper 1027, the silver 833, the lead 487, and the tin 444. Similar differences will be found with regard to almost every kind of matter.

The general experiment, as I have already stated, by which the quantities of caloric which bodies contain are determined, is mixing together equal weights of two different kinds of matter, at different temperatures, and observing the temperature which is produced. If we take equal portions of the same kind of matter, one pound for example at 50°, and another at 100°, and mix them, guarding at the same time against any error from the abstraction or communication of caloric by the vessel, or by the atmosphere, the temperature of the whole will be the exact arithmetical mean between the two temperatures, that is in the present example 75. The pound at 100 will have parted with half its excess of caloric, or 25 degrees, and this added to the pound at 50°, will raise its temperature precisely 25 degrees. This proves that the quantity of caloric which occasions a certain extent of change in the temperature of one portion of a body, will produce exactly the same change in the temperature of another equal portion of the same body, and consequently equal weights of it at any temperature will contain equal quantities of caloric.

But, when the same experiment is made with two different bodies, the result is entirely different, the temperature produced never being the mean of the respective temperatures. Thus, if one pound of water at 156° be mixed with one pound of mercury at 40°, the resulting temperature is not the mean 98, but is not less than 152. This proves that the change of temperature produced in the one by a certain quantity of caloric, is entirely different from that produced

in the other by the same quantity; for the water in this experiment having had its temperature reduced from 156° to 152°, has lost a quantity of caloric producing in it a change of 4 degrees, but this quantity communicated to the mercury has raised its temperature from 40° to 152°, or produced a change in it of not less than 112°. The quantity of caloric, therefore, necessary to raise the temperature of one pound of water 4 degrees, is sufficient to raise that of an equal weight of mercury 112°, or the quantity raising the temperature of the one of these fluids one degree, will raise that of the other 28°. This, it is concluded, will be the case at every temperature, and therefore at any point in the scale of heat, the quantity of caloric contained in water is to that contained in the same weight of mercury as 28 to 1.

If the experiment is varied, by mixing water at a low and mercury at a high temperature, the result is the same, or the change produced in the temperature of the mercury is to that produced in the temperature of the water as 28 to 1. If one pound of quicksilver at 156° be mixed with one pound of water at 40°, the temperature produced is 44°; the mercury has lost a quantity of caloric, which has reduced its temperature 112 degrees, and this communicated to the water has raised its temperature only 4°.

In this manner, when equal weights of two different bodies are mixed together, the temperature produced is always nearer to the temperature of that body which contains the largest quantity of caloric, because it requires the largest quantity to produce a

change in its temperature. The proportion is also indicated by the experiment, the comparative quantities of caloric contained in the two bodies being in the inverse ratio to the change of temperature of each by their mixture. Taking water as a substance usually employed in the experiment, and as the standard to which the others are referred, the following general formula has been given. Multiply the weight of the water by its change of temperature. Do the same for the other substance. Divide the first product by the second. The quotient expresses the comparative quantity of caloric contained in that substance, the quantity contained in water being accounted 1. Or more generally, and without any reference to water being employed, but merely from two bodies being mixed in equal weights — multiply the weight of each body by the number of degrees between its original temperature and the common temperature obtained by their mixture. The capacities of the bodies will be inversely as the products.

When, instead of comparing the quantities of caloric which equal *weights* of different bodies contain, we compare the quantities contained in equal *volumes*, we still find a difference exists. Thus it is established by experiment, that the quantity of caloric necessary to raise the temperature of a given volume of water any number of degrees, is to that necessary to raise an equal volume of mercury the same number of degrees as rather more than 2 to 1; and this consequently is the proportion between the quantities of caloric in these bodies estimated by their volumes.

The comparative quantities of caloric in bodies are usually estimated by their weights, it being in general less difficult to ascertain these with accuracy than to ascertain their volumes.

In some cases water cannot be employed in such experiments, from the substance, the capacity of which is to be ascertained, exerting a chemical action, by which the existing capacity is altered, and caloric either evolved or absorbed. In such cases Dr Irvine employed the medium of a third body, generally pounded glass; adding to a given weight first of the water, and secondly of the substance whose capacity was to be ascertained, a quantity of glass sufficient to change their temperature the same number of degrees. The capacities were then as the weights of glass added *.

The method which Wilcke employed, though essentially the same with that now described, was in the mode of performing it somewhat different. His experiments were restricted to substances existing in the solid state. A pound of such a substance, of a metal for example, was accurately weighed; it was then suspended by a thread in a vessel of boiling water, in which a thermometer was placed, to mark the temperature with more precision. An equal quantity of water, in the present example, one pound, at the temperature of 32°, was put into a tinned iron vessel. The heated body was immediately removed from the vessel of boiling water, and was suspended in the cold

* Chemical Essays, p. 87.

water, taking care that it should not touch the sides or bottom. A thermometer with a centigrade scale, each degree being such that 4ths or even 8ths could be distinguished on it, was put into the fluid, and the temperature was taken when it had become uniform through the fluid, and the same as that of the solid suspended in it. The caloric given out by the hot body, was of course communicated to the cold fluid, the changes occasioned in the temperature of the one by the abstraction, and in that of the other by the addition of this caloric were thus discovered, and the quantity of caloric contained in the body subjected to experiment compared with that of the water was easily found; the same formula applying to this method as to the preceding one, though that which Wilcke employed was somewhat more complicated *.

It is obvious, that the accuracy of these experiments depends on the assumption, that the caloric abstracted from the hot body is communicated entirely to the colder, and that the latter receives caloric from no other source. It is impossible, however, that these requisites should be perfectly attained. In the mode of mixture, if the cold substance be added to the hot one, it must receive a portion of caloric not only from it, but likewise from the vessel in which it is contained; or if, as is more usually the case, the hot body be added to the cold, the caloric it gives out will not be

* Translation of Wilcke's Paper, from the Memoirs of the Royal Academy of Sciences of Stockholm, for 1781, in the *Journal de Physique*, t. xxvi. p. 250.

communicated entirely to the latter, but will in part be abstracted by the vessel. It is difficult also, or scarcely possible, to abstract entirely the agency of the atmosphere, which, as one of the bodies is always at a temperature superior to it, will carry off part of the caloric. But the portions of caloric thus withdrawn from the mixture by these causes, will vary according to the quantities of the bodies used in the experiment,—the degree of agitation by which they are mixed,—the celerity with which different bodies part with their caloric,—their specific gravities,—and their miscibility with water. Even the size and shape of the vessel, and the composition of the matter of which it consists, will influence the result; and hence have arisen the differences in the experiments of different chemists. Dr Crawford, who made more experiments on this subject than any other chemist, has, in his excellent treatise, pointed out the principal circumstances which require to be attended to. He found it necessary to determine the precise effect of the vessel on the result of the experiment, by ascertaining the quantity of caloric it required to produce a certain change in its temperature; and to calculate the quantity of caloric communicated to the air, by observing the progress of cooling, and the time which elapsed before a common temperature was established; and he also adds the necessary cautions, by which the other sources of error may be best obviated *.

In the method employed by Wilcke, these sources

* Treatise on Animal Heat, p. 96.

of error must have less influence than in the method by mixture, as the influence of the air can be more effectually excluded. This method, however, cannot well be applied to liquids; and with regard to these, the mode by mixture is at the same time less liable to error, than it is with regard to solids, as two fluids can be mixed together with more facility than a solid or a liquid, and their common temperature will be sooner formed.

Another method of estimating the comparative quantities of caloric, has been employed, founded on the fact, that ice or snow, in melting, absorbs always a uniform quantity of caloric: and therefore, by placing a hot body in contact with ice, so that the whole of the caloric it gives out in the reduction of its temperature to 32°, shall be communicated to the ice, and spent in melting it, we may determine, from the quantity of water thus formed, the portion of caloric which has been communicated by the hot body. Wilcke, to whom this fact was known, conceived the idea of employing the melting of ice or snow, as a method of measuring, or at least of comparing the quantities of caloric in bodies; all that is necessary, says he, being "to find, by experiment, how much "soft snow is necessary to cool different bodies, from "a certain determined temperature, to that of melting snow or ice; for the whole heat which the body loses in this reduction ought to be found in the "melted snow; and thus the quantity may be known "from the quantity melted, or the quantity of wa-

" ter produced *." In attempting, however, to carry this into execution, he found, he says, unexpected difficulties; the principal of which was that of determining, with accuracy, the quantity of water produced, as much of it remained mixed with the portion of unmelted snow; and hence he relinquished this method, for that which has been already described.

Lavoisier and La Place, however, aware of the errors attending the mode by mixture, directed their attention to this other method, and they contrived an instrument, the Calorimeter, by which the experiment can be performed, as they believed, with more accuracy.

This instrument of which a representation is given, Plate VII. Fig. 51, consists of three vessels, A, B, C, adapted to each other, and inserted the one within the other, so as to leave a cavity between the sides of each.

The smallest or innermost, A, is a cage of iron network, and is designed to contain the body which is to be subjected to experiment. It is supported by several iron bars, which are attached to the internal cavity of the second or middle vessel B. This one is designed to contain the ice, from the melting of which the quantity of caloric given out by the body in the first vessel is to be estimated. The ice is broken into small pieces; these are supported on an iron grating at the bottom, through which the water filters, and is conveyed off by a pipe with a stop-cock *a*, which comes

* *Journal de Physique*, t. xxvi. p. 258.

from the bottom of the vessel. It has a double cover *b*, also adapted to it, capable of containing ice; the under part of this being perforated, so that the water which may be formed from the melting of any of the ice it contains, may drop into the cavity itself. The third, or outer vessel, C, is similar in its construction to the second, and, like it, is to be filled with pounded ice, when the experiment is to be performed. The design of it is to prevent the agency of the external atmosphere. It would be inconvenient to operate with this instrument only when the temperature of the atmosphere is at 32°; but it is obvious, that at temperatures above or below this, a heating or cooling agency would be exerted by the exernal air on the ice, which is designed to be exposed to the hot body only. If the atmosphere were above 32°, it would communicate caloric to the ice, and of course would contribute to its fusion, and prevent us from considering the quantity of water produced as a measure of the quantity of caloric which the hot body had given out; or if below 32°, it would abstract caloric, and lessen the quantity that would otherwise be melted. The design of the outer vessel is to obviate these sources of error, and surround the ice in the middle vessel with a medium at the temperature of 32°. It also has a double cover D, containing pounded ice, to serve the same purpose, and a tube and stop-cock *c*, by which the liquid can be withdrawn.

The method of performing the experiment with this apparatus is obvious. The substance on which we are to operate is raised to a certain temperature,

which is ascertained, and is then suspended in the innermost cavity, the middle cavity having been previously filled with pounded ice pressed down, so that no void spaces shall remain, and drained so that no water remains mixed with the ice. The caloric it gives out in falling to 32°, is communicated to the ice in this cavity, and melts more or less of it. Lavoisier and La Place calculated from experiment, that one pound of ice in melting absorbs a quantity of caloric which would raise the temperature of water 135 degrees of Fahrenheit, and proceeding on this calculation, by withdrawing the quantity of water produced, and weighing it, it was easy to ascertain the quantity of caloric which the substance in the reduction of temperature it had suffered had given out; its weight being exactly proportional to the quantity of caloric which the body had given out in its reduction of temperature. By repeating the experiment on different bodies, the comparative quantities of caloric they evolve in passing from one temperature to another, and of course the comparative quantities they contain, were determined. Liquids were introduced in a glass matrass, which was suspended in the cage; the quantity of caloric which the glass would give out, being ascertained by a previous experiment, and airs were operated on, by passing them through a spiral tube, which was fixed in the middle vessel, a thermometer being placed at each extremity of it, to ascertain the temperature of the air as it entered and passed out.

These experiments should be made at a tempera-

ture at or a little above 32°, as, below that, the contents of the outer vessel may be entirely frozen, be cooled, and abstract caloric from the middle vessel. Nor should the temperature be more than 10 or 12 degrees above that; for the air included in the instrument, being then heavier than the external air, descends, issues by the tube at the bottom through which the water runs off; and thus a current of air is formed which communicates heat to the ice. The nearer, therefore, the temperature of the external atmosphere is to 32°, the experiment will be more accurate *.

The mode of operating by this instrument is extremely simple, and it is not exposed to those sources of error which attend the method by mixture. It has another advantage over the latter, that it can be applied to those bodies, which, when mixed with each other, exert a mutual chemical action, and to which the method by mixture is not easily applicable, as, by such actions, the quantities of caloric which the bodies contain are changed, and in the very progress of the experiment, their temperatures are from this cause augmented or reduced.

It has been supposed, however, to be liable to some other errors, which have rendered it doubtful, whether, on the whole, it is more accurate than the other. Two circumstances have in particular been pointed out by Mr Wedgwood as influencing the results.

The first is, that part of the water formed by the melting of the ice, is retained by capillary attraction

* *Mémoires de l'Acad. des Sciences*, 1782, p. 355.

in the interstices of the unmelted ice; and hence the quantity that passes off by the tube, at the bottom of the apparatus, is not the proper measure of the quantity actually produced. Lavoisier and La Place were aware of this source of error, but they supposed it could not be of any importance, or might be obviated by strewing the pounded ice in the calorimeter, in thin layers, and allowing it to stand for some time in an atmosphere above 32°, before the experiment was begun. It would thus have imbibed all the water that it could retain by capillary attraction; and therefore the quantity would be the same at the beginning and at the end of the experiment. It is obvious, however, that as in the progress of the experiment, the quantity of the ice, and its arrangement in the vessel must be altered, the portion of water retained by capillary attraction will not be precisely the same, though it is difficult to say to what extent this source of error may operate.

Another, perhaps more important, arises from a singular fact, discovered by Mr Wedgwood, that the operations of thawing and freezing actually go on in the apparatus at the same time, or that part of the water which is melted in the upper part of the middle vessel, in filtrating through the ice, again returns to the solid state. Mr Wedgwood has very clearly shewn, that this is the case, especially in the lower parts of the apparatus, the fragments of ice thrown in loose being frozen together, so that a passage made through the loose ice is soon nearly filled up *. It is no doubt ow-

* Philosophical Transactions, vol. lxxiv. p. 376.

ing to the cohesive attraction exerted by the surfaces of the fragments of ice to the water at 32° which is applied to them, and is a phenomenon of precisely the same kind as the promoting the crystallization of a salt which is in solution, by the contact of a crystal of that salt. It must render the results of experiments made with this apparatus, somewhat uncertain. In Mr Wedgwood's experiments, its influence appears to be considerable, from the smallness of the heated body which he introduced into the ice, and by which a small quantity of water would be formed, compared with the surface of unmelted ice over which it had to pass; while, in the experiments of Lavoisier and La Place, the results are described as being always nearly uniform, probably from this source of error being rendered less important by the larger quantities subjected to experiment. Still if any of the water be congealed, even although there should be a uniformity in the experiments; in other words, although this quantity should be always very nearly the same, if allowance be not made for this, it must lead to an erroneous conclusion as to the quantity of caloric which the heated body has given out.

Since different bodies, whether in equal weights or in equal volumes, contain, at the same temperature, very different quantities of caloric, there must be some cause by which this difference is produced; something in the relation of bodies to caloric, varying in its intensity in each, by which one requires a quantity different from that required by others, to produce the same change in its temperature.

The property itself has been termed the capacity of bodies for heat, or, adapting the expression to the established nomenclature, the capacity of a body for containing caloric. This phrase is not perhaps free from ambiguity, and it has accordingly been much misunderstood. Yet if it be considered as expressing merely the general fact, that different bodies contain, at equal temperatures, and in equal quantities of matter, different quantities of caloric, or rather, as denoting the property by which they do so, without its being understood to convey any idea as to the cause of that fact or property, the expression cannot lead into error. It is in this sense that it is employed by those philosophers, to whom we are indebted for our knowledge of this subject, and by no means as expressing mere capaciousness as some have supposed. The caloric thus contained in bodies in quantities peculiar to each, was named by Wilcke their specific heats, by Crawford their comparative heats. The phrase Specific Caloric, is now generally used to express it, and as applied to any particular body, denotes the quantity of caloric which any weight of it at a given temperature contains, compared with the quantity which another body in the same weight, and at the same temperature, contains. Thus the specific caloric of water is said to be to that of milk as 1000 to 999. The term Relative Heat, was employed by Wilcke to denote the quantity of caloric contained in bodies, measured not by their weight but by their volumes.

Of the relation between this property, the agent on which it operates, and the state with regard to tempe-

rature to which it gives rise, the following clear statement is given by Dr Crawford; the term heat in his language being synonymous with caloric: "The temperature, the capacity for containing heat, and the absolute heat contained, may be distinguished from each other in the following manner: The capacity for containing heat, and the absolute heat contained, are distinguished as a force from the subject upon which it operates. When we speak of the capacity, we mean a power inherent in the heated body; when we speak of the absolute heat, we mean an unknown principle which is retained in the body by the operation of this power; and when we speak of the temperature, we consider the unknown principle as producing certain effects upon the thermometer." The capacity for containing heat may continue unchanged, while the absolute heat is varied indefinitely, and by every addition of absolute heat in this case, the temperature will be increased, or by its abstraction will be reduced. The temperature of a body, therefore, depends on its capacity, and on the quantity of heat communicated to it, and from a variation of either, a change in the temperature must result. If the capacity be enlarged, the quantity of caloric remaining the same, the temperature must fall; if it be diminished, the temperature will rise, in precisely the same way as if the capacity had remained constant, and caloric had been communicated or withdrawn.

The inquiry will naturally suggest itself, To what cause is this difference in the capacities of bodies to be ascribed? or, to take the more general statement of the

question, What is the nature of that property by which one body requires more caloric than another, to produce the same temperature?

In prosecuting this investigation, the general fact is soon presented to us, that there is an intimate connection between the capacities of bodies for caloric, and their state with regard to rarity or density. We find, on examination, that those bodies which contain the least quantity of caloric at a given temperature, or which, in other words, have the leaſt capacity, are those of greateſt density, such as the metals, and their more dense combinations; and, on the other hand, substances of the greatest rarity—the different elastic fluids or airs, are those which have the greatest capacities for caloric. Even of these, the one which is the most rare, and which, indeed, is the substance of greatest rarity, whose gravity we can ascertain, is that which has the largest capacity of any known body.

Not only is there this intimate connection between the density of a body and its capacity; we can even change the capacity by changing the density; in particular, by rarifying a body we produce such a change in its capacity that it requires more caloric to keep up its existing temperature. This is conspicuous in those substances which are most susceptible of rarefaction, the aëriform fluids. When any species of air is rarified by the air-pump, its temperature falls, obviously from the increased rarity enabling the air to contain a larger quantity of caloric at a certain temperature, and as this caloric cannot be immediately absorbed from the surrounding bodies, the tempera-

sure of the air suffering rarefaction must be reduced. On the contrary, by compressing any aëriform fluid, caloric is extricated, the power of containing it, or the capacity, being diminished by the reduction of volume. The changes of temperature from these causes, it has been shewn by Mr Dalton, are greater than what they appear to be on experiment, from the surface of the contiguous vessel rapidly absorbing or yielding caloric, and thus quickly checking the actual change *. To this cause also is undoubtedly to be referred a fact discovered by Mr Watt, and which otherwise appears anomalous, which has indeed appeared so much so to Berthollet, that he is unwilling to admit it † : "That "the latent heat of steam," (which, as we shall afterwards shew, depends on the capacity), "is less when "it is produced under a greater pressure, or in a more "dense state, and greater when it is produced under a "less pressure, or in a less dense state ‡."

When, by other means, we have changed the volume of a body without materially altering its nature, we change at the same time its capacity for caloric. A very striking fact of this kind is stated by Mr T. Wedgwood. The clay of which the pyrometer pieces are prepared, he found has its capacity diminished one-third, by being burnt to 120° of the pyrometrical scale, and thus reduced to about one-half of its bulk, and as it loses in weight he adds, little more

* Manchester Memoirs, vol. v.

† Chemical Statics, vol. i. p. 415.

‡ Philosophical Transactions, vol. lxxiv. p. 335.

than two grains in a pound, the diminution of capacity can only be ascribed to its condensation *. Lastly, when we combine substances together, if the combination be attended, as it frequently is, with an increase of density, it is also in this case attended with a diminution of capacity, as is well exemplified in the combinations of alkohol, or of sulphuric acid, with water.

So far the connection appears intimate between the rarity of bodies and their capacities. These, however, are by no means proportional to each other. On the contrary, the deviations are considerable and numerous. Water, for example, has a capacity to that of mercury as 28 to 1, while the difference in their specific gravity is only as 1 to 13. Alkohol is considerably less dense than water, yet instead of having a greater capacity, it has a less one, in the proportion of 602 to 1000. A number of similar examples might be stated, which prove that the capacities of bodies can never be regarded as inversely as their densities.

It cannot be doubted but that this is owing to the peculiar attraction by which caloric is contained in bodies. Its particles being mutually repellent, its tendency is to diffuse itself equally over space, and did no foreign power operate, it would be contained in all bodies, the temperatures being alike, in quantities proportioned to the spaces they occupy. But, when introduced into bodies, some attraction must be exerted towards it; this modifies the law which would otherwise be

* Philosophical Transactions for 1792, p. 280.

observed, and being probably different in its intensity in different bodies, gives rise to the specific quantities which they contain. The exertion of such an attraction may not only be inferred with probability, but is established by the fact proved by Dr Crawford, that a vacuum has even less capacity for caloric than atmospheric air *.

This is probably the just view of this interesting and difficult question,—the cause of the different capacities of bodies for caloric. The tendency of caloric is to diffuse itself equally over space, and of course to exist in bodies in quantities proportioned to the void spaces between their particles, or rather to the distances to which, by its elasticity, and their relative force of cohesion, it is capable of separating them at a given temperature. But it does not exert this elasticity undisturbed; an attraction must be exerted towards it by the particles between which it is interposed, and by this attraction it may be condensed; and the attraction, it may be presumed, being different, as exerted by different bodies, hence may arise the difference in the quantity of it contained in different bodies at any given temperature. That the attraction alone, however, is not the cause, is evident from the fact that by increasing the quantity of matter in a given volume, as by compression, so far from increasing the quantity of caloric, which, at a given temperature, may be contained in that volume, we actually diminish it, and hence render a portion sensible.

* Treatise on Animal Heat, p. 266.

At the same time, in the exertion of this specific attraction, we observe none of the usual laws of chemical affinity; the phenomena attending the communication or abstraction of caloric are totally dissimilar to those of chemical combination; it exists in bodies with its properties unaltered, the *quantity* they contain only being determined by the attraction they exert towards it.

It was the observation of this dissimilarity to chemical union, and likewise of the fact that in general rare bodies contain more caloric at a given temperature than those which are more dense, that led to the conception from which the term Capacity originated, that caloric is rather mechanically diffused through bodies than chemically combined with them; that it merely fills the interstices between their particles; or according to the comparison which has often been made, that it exists in them in a manner somewhat similar to that in which water is contained in a sponge.

It was soon discovered, indeed, that this view was incorrect; but still as the term capacity had been introduced, and as no better one occurred, it was retained to express the unknown cause or property in bodies by which they contain at given temperatures their respective quantities of caloric. I have already stated, that it is not strictly just, and the ambiguity attached to it has undoubtedly given rise to the mistakes on this subject, and the misapprehension of the theory which have been so frequent among chemists. Yet it would be difficult to find a term less exceptionable. That of Affinity would equally lead

to misconception, as suggesting the false idea that the state in which caloric exists in bodies is similar to that state of combination into which substances enter from the exertion of energetic chemical attractions.

If it be recollected that the term Capacity for Caloric denotes merely the property by which bodies at given temperatures contain their respective quantities of caloric, and which is different in its intensity in each, there can be no objection to its use. This is the sense attached to it by Irvine and Crawford. They employed it not to denote any peculiar cause, mechanical or chemical, but simply as the expression of the general fact. Understood in this manner, it can lead into no error, and thus defined it is scarcely possible to misapprehend the beautiful theory unfolded by the researches of these philosophers.

It will be obvious, from the nature of the experiment by which the capacities of bodies are ascertained, that they are merely comparative. We discover only how much caloric a body gives out or absorbs during a certain change of temperature; and by observing at the same time the change of temperature which the body from which it has received, or to which it has given this caloric, suffers, we ascertain the comparative quantities necessary to produce equal changes of temperature in these bodies. But we do not learn the proportion which the quantity in each bears to the whole caloric it contains, and therefore the capacities are to be regarded as merely comparative. Hence it becomes necessary to assume an arbitrary standard, to which the others are referred. Wa-

ter is taken as this standard. Its capacity is stated as 1000, and to this the capacities of other bodies, whether greater or less, are referred. Thus the capacity of hydrogen gas is stated as 21.400; implying, that if at any given temperature, a certain weight of water contain 1000 parts of caloric, the same weight of hydrogen gas, at the same temperature, will contain 21.400 such parts. The capacities have sometimes been estimated, by comparing bodies in equal volumes, and sometimes by comparing them in equal weights. The latter, however, can be done with most accuracy; and it is also proper to refer the quantity of caloric contained in a body to the quantity of matter, as it is by the action of this matter on it that the proportion of caloric is regulated. The capacities, as they relate to equal volumes, may be easily found by multiplying the number expressing the capacity or specific caloric of any substance as estimated by its weight, by the number which denotes the specific gravity of that substance, the product being the specific caloricestimated by the volume.

From these observations, the following table of capacities will be easily understood, the capacity of water being taken as the standard 10,000, to which the capacities of the other bodies in equal weights are referred. As the capacities of bodies are different as they exist in the solid, liquid, or aëriform state, I have subdivided the table according to these forms *.

* It is necessary to state the authorities from which this table is drawn up. Dr Crawford paid the greatest

TABLE OF CAPACITIES.

Gases.

1. Hydrogen gas,	21.4000 C.
2. Oxygen gas,	4.7490 —
3. Atmospheric air,	1.7900 —
4. Aqueous vapour,	1.5500 —
5. Carbonic acid gas,	1.6454 —
6. Nitrogen gas,	7936 —

attention to this subject, and made the most extensive series of experiments on the capacities of different bodies. His labours, therefore, form the basis of the table. The capacities of a few substances were likewise ascertained by Dr Irvine. To Wilcke we are indebted for experiments on the capacities of a number of the metals; and to Gadolin for a knowledge of those of some other bodies, particularly of saline solutions. Lavoisier and La Place ascertained the capacities of several substances by the calorimeter; and Meyer, in his late experiments on the conducting power of the different kinds of wood, determined at the same time their capacities. Besides these, Magellan gave a table of specific heats, communicated to him by Mr Kirwan; but with regard to these there is considerable obscurity. A number of them are those which were given by Dr Crawford, in the first edition of his work on heat, and which he afterwards corrected as being erroneous. But there are also several others which were not in Dr Crawford's table. These, it is to be presumed, were ascertained by Mr Kirwan; though, as this is not certain, and as they are given by Magellan, I have

Liquids.

7.	Solution of carbonate of ammonia,	1.8510	M.
8.	——— of brown sugar,	1.0860	—
9.	Alkohol, (15.44) -	1.0860	—
10.	Arterial blood, - -	1.0300	C.
11.	Water, - -	1.0000	
12.	Cows milk, - -	9999	C.
13.	Sulphuret of ammonia, -	9940	M.
14.	Solution of mur. of soda, 1 in 10 of water,	9360	G.
15.	Alkohol, (9.44) - -	9300	Ir.
16.	Sulphuric acid, diluted with 10 of water,	9250	G.
17.	Solut. of muriate of soda in 6.4 of water,	9050	—
18.	Venous blood, - -	8928	C.
19.	Sulphuric acid, with 5 parts of water,	8760	G.
20.	Solution of muriate of soda in 5 of water,	8680	—
21.	Nitric acid, (39) - -	8440	M.
22.	Solut. of sulphate of magnesia in 2 of water,	8440	—

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referred them to his authority. From the imperfect account which we have of them, their accuracy is perhaps more doubtful than that of the others. The discordant results, however, which are so frequent among all the experiments which have been made on the subject, sufficiently prove the difficulties of this investigation, and that the numbers are to be regarded rather as approximations to the real capacities than actual expressions of them. The initial letter of the name of each author is annexed to the numbers of the substances, the capacities of which he ascertained; and where a difference exists in the capacity of any body, as ascertained by different chemists, I have always given it according to each, with a reference to the different statements, that the authorities may be compared, and that selected on which it may be supposed most reliance is to be placed.

23.	Solution of muriate of soda in 8 of water,	8320	M.
24.	Solution of mur. of soda in 3.33 of water,	8200	G.
25.	——— nitrate of potassa in 8 of water,	8167	L.
26.	——— muriate of soda in 2.8 of water,	8020	G.
27.	——— mur. of ammonia in 1.5 of water,	7980	M.
28.	——— muriate of soda saturated, or in 2.69 of water,	7930	G.
29.	——— supertartrite of potassa in 237.3 of water,	7650	M.
30.	Solution of carbonate of potassa,	7590	—
31.	Colourless sulphuric acid, (51. 55, 56, 57)	7580	—
32.	Sulphuric acid, with 2 parts of water,	7490	G.
33.	Solution, sulphate of iron in 2.5 of water,	7340	M.
34.	Solut. of sulphate of soda in 2.9 of water,	7280	—
35.	Olive oil,	7100	—
36.	Water of ammonia, spec. gr. 0.997,	7080	—
37.	Muriatic acid, specific gravity 1.122,	6800	—
38.	Sulphuric acid, 4 parts with 5 of water,	6631	L.
39.	Nitric acid, specific gravity 1.29895,	6613	—
40.	Solution of alum in 4.45 of water,	6490	M.
41.	Mixture of nitric acid with lime, $9\frac{1}{3}$ to 1,	6189	L.
42.	Sulphuric acid, with an equal wt. of water,	6050	G.
43.	——— ——— 4 parts with 3 of water,	6031	L.
44.	Alkohol, (9.15)	6021	C.
45.	Nitrous acid, specific gravity 1.354,	5760	M.
46.	Linseed oil,	5280	—
47.	Spermaceti oil, (53)	5000	C.
48.	Sulphuric acid, with $\frac{1}{2}$ of water,	5000	G.
49.	Oil of turpentine, (52)	4720	M.
50.	Sulphuric acid, with $\frac{1}{4}$ of water,	4420	G.
51.	Sulphuric acid, (31. 55, 56, 57)	4.290	C.
52.	Oil of turpentine, (49)	4000	Ir.
53.	Spermaceti oil, (47)	3990	M.
54.	Red wine vinegar,	3870	—
55.	Sulphuric acid, concentrated and colourless, (31)	3390	G.
56.	——— specific gravity 1.87058,	3345	L.
57.	——— (31.51)	3330	Ir.
58.	Spermaceti melted,	3200	—
59.	Quicksilver, specific gravity 13.30,	330	M.
60.	———	290	L.

61.	Quicksilver,	290	W.
62.	———	280	Ir.

Solids.

63.	Ice,	9000	M.
64.	——	8000	Ir.
65.	Ox hide, with the hair,	7870	C.
66.	Sheeps lungs,	7690	—
67.	Beef of an ox,	7400	—
68.	Scotch fir wood,	6500	M.
69.	Lime-tree wood,	6200	—
70.	Spruce-fir wood,	6000	—
71.	Pitch-pine wood,	5800	—
72.	Apple-tree wood,	5700	—
73.	Alder wood,	5300	—
74.	Sessile-leaved oak,	5100	—
75.	Ash wood,	5100	—
76.	Pear-tree wood,	5000	—
77.	Rice,	5060	C.
78.	Horse beans,	5020	—
79.	Dust of the pine-tree,	5000	—
80.	Pease,	4920	—
81.	Beech,	4900	M.
82.	Hornbeam wood,	4800	—
83.	Birch wood,	4800	—
84.	Wheat,	4770	C.
85.	Elm,	4700	M.
86.	White wax,	4500	G.
87.	Pedunculated oak wood,	4500	M.
88.	Prune-tree,	4400	—
89.	Ebony wood,	4300	—
90.	Quicklime, with water, in the proportion of 16 to 9,	4391	L.
91.	Barley,	4210	C.
92.	Oats,	4160	—
93.	Charcoal of birch-wood, (99)	3950	G.
94.	Carbonate of magnesia,	3790	—
95.	Prussian blue,	3300	—
96.	Quicklime satur. with water, and dried,	2800	—
97.	Pit-coal,	2777	C.
98.	Artificial gypsum,	2640	G.
99.	Charcoal, (93)	2631	C.

100.	Chalk, (108)	2564 C.
101.	Rust of iron,	2500 —
102.	White clay,	2410 G.
103.	White oxide of antimony washed,	2272 C.
104.	Oxide of copper,	2272 —
105.	Quicklime, (107)	2239 —
106.	Muriate of soda in crystals,	2260 G.
107.	Quicklime, (105)	2168 L.
108.	Chalk, (100)	2070 G.
109.	Crown glass,	2000 Ir.
110.	Agate, specific gravity 2648,	1950 W.
111.	Earthen-ware,	1950 M.
112.	Crystal glass without lead,	1929 L.
113.	Cinders,	1923 C.
114.	Sulphur,	1890 Ir.*jr*
115.	Ashes of cinders,	1855 C.
116.	White glass, specific gravity 2.386,	1870 W.
117.	White clay burnt,	1850 G.
118.	Black lead,	1830 —
119.	Sulphur,	1830 M.
120.	Oxide of antimony, nearly free of air,	1666 C.
121.	Rust of iron, ditto, ditto,	1666 —
122.	Ashes of elm-wood,	1402 —
123.	Iron, (125. 127, 128. 132)	1450 Irv.
124.	Oxide of zinc, nearly freed from air,	1369 C.
125.	White cast iron,	1320 G.
126.	White oxide of arsenic,	1260 —
127.	Iron, (123. 132)	1269 C.
128.	Iron, specific gravity 7876,	1260 W.
129.	Cast iron abounding in plumbago,	1240 G.
130.	Hardened steel,	1230 —
131.	Steel softened by fire,	1200 —
132.	Soft bar iron, specific gravity 7.724,	1190 —
133.	Brass, specific gravity 8356, (135)	1160 W.
134.	Copper, specific gravity 8.785, (136)	1140 W.
135.	Brass, (133)	1123 C.
136.	Copper, (133)	1111 —
137.	Sheet iron,	1099 L.
138.	Zinc, specific gravity 7154, (143)	1020 W.
139.	White oxide of tin, nearly free of air,	990 C.
140.	Cast pure copper, heated between charcoal, and cooled slowly, spec. gr. 7907,	990 G.

141.	Hammered copper, spec. gr. 9150,	970 G.
142.	Oxide of tin,	960 M.
143.	Zinc, (138)	943 C.
144.	Ashes of charcoal,	909 —
145.	Sublimed arsenic,	840 G.
146.	Silver, specific gravity 10.001,	820 W.
147.	Tin, (152)	704 C.
148.	Yellow oxide of lead,	680 —
149.	White lead,	670 G.
150.	Antimony,	645 —
151.	Antimony, specific gravity 6107,	630 W.
152.	Tin, specific gravity 7380, (147)	600 W.
153.	Red oxide of lead,	590 G.
154.	Gold, specific gravity 1904,	500 W.
155.	Vitrified oxide of lead,	490 G.
156.	Bismuth, specific gravity 9861,	430 W.
157.	Lead, specific gravity 1145,	420 W.
158.	——	352 C.

On the subject of capacities, it is an interesting question, whether they are permanent; in other words, are they the same at all temperatures? Will the quantity of caloric which raises the temperature a certain number of degrees at one part of the thermometrical scale, suppose at the medium temperature of the atmosphere, raise it the same number of degrees at any other, even the most remote temperature, either higher or lower than this? It is obvious, that this may not be the case, but that the capacity may be irregular, may be increased or diminished, by an alteration of temperature, or that, at different parts of the scale of heat, the change in the actual temperature, from the communication of a given quantity of caloric, may be either greater or less than what it is at lower temperatures.

In considering this question, it is necessary to remark, that the capacities of bodies are altered when they change their forms. When they pass from the solid to the fluid, or from the fluid to the aëriform state, their capacities are enlarged, and of course are diminished when they suffer the reverse changes. But, with this exception of change of form, are the capacities of bodies permanent, or, on the contrary, do bodies require, at different temperatures, different quantities of caloric to produce equal changes?

This was made the subject of experiment by Dr Crawford. The experiment consisted in mixing together equal quantities of the same body at different temperatures. If the capacity at all temperatures between these were uniform, it is obvious, that the temperature formed would be the precise arithmetical mean; for, on that supposition, the quantity of caloric abstracted from the hotter portion, and communicated to the colder, would raise the temperature of the one just as much as it reduced that of the other. But if the capacity were not permanent, if it was either augmented or diminished by a rise or fall of temperature, there would be a deviation greater or less from the arithmetical mean. If the capacity, for example, were greater at a high than at a low temperature, then the temperature resulting from mixing the two portions together would be above the arithmetical mean, as the quantity of caloric yielded by the hotter to the colder, would not reduce its temperature so much as it would raise that of the other; and, on the other hand, if the capacity were less at the high tem-

perature, for a similar reason, the resulting temperature would be below the arithmetical mean.

To determine this, Crawford mixed together equal portions of hot and cold water; the temperature of the mixture was the mean between the two; and hence he concluded justly, that the capacity of water is permanent in all temperatures between its freezing and boiling points. He then extended his experiments to many other substances, especially to the metals, and some of their compounds, and though the results did not correspond accurately with the supposition of a permanence of capacity, yet they agreed more nearly with it than with any other: "Hence we may "conclude in general," he adds, "that the capacities "of bodies which retain the same form, are permanent in the intermediate temperatures between the "freezing and boiling points of water; and we may "infer by induction, that the same law obtains "throughout the whole of the scale of heat *."

Admitting, what is not improbable, that there is no sensible deviation from permanence of capacity in that part of the scale of temperature intermediate between the freezing and boiling points of water, what reason is there to infer that the same permanence will continue at all temperatures? There is absolutely none. Not only, however, is the conclusion unsupported; it appears to me far from being improbable, that a change of capacity may arise from

* Treatise on Animal Heat, p. 65.

changes of temperature, when these are considerable; and if the view which I have given of the cause of the difference of capacities in bodies be just, it is even probable that such a change must actually take place. If the quantity of caloric contained in bodies, be in part proportioned to their rarity, or to the interstices into which it may be admitted, since an increase of temperature is accompanied by expansion, it seems necessarily to follow, that it must give rise to some enlargement of capacity, or that the body in this state must admit more caloric, proportioned to its temperature, than when in a denser state. When the volume of a body is increased, without the direct application of caloric, as in the gases by withdrawing pressure, their capacities are augmented. Is it not, therefore, reasonable to believe, that when the volume is augmented by the operation of caloric itself, there should still be an augmentation of capacity? Indeed, in the former case, the augmentation of volume, and ultimately of capacity, are really owing to the operation of caloric; for the withdrawing pressure only removes an obstacle to its exertion; and the fact, therefore, at once proves, that when the volume of a body is materially enlarged, by the operation of caloric itself, the capacity is also increased.

The influence of the specific attraction of bodies to caloric, in determining the capacity, may indeed be still greater than that of the volume; but still the other must operate to a certain extent, and this extent, it is not possible *a priori* to determine, for we do not know the relative influence of these two causes in gi-

ving rise to the specific capacity, and still less do we know the amount of expansion through the whole scale of temperature. It is evident, that this reasoning is not in the slightest degree weakened by the fact, admitting it to be established, That the capacities are permanent between the freezing and boiling points of water; for this part of the scale of temperature must be so inconsiderable, when compared with the whole, that no just inference can be drawn from any fact relating to it, as to what will happen in other parts of the scale, and the degree of expansion which bodies experience in passing through it must be so inconsiderable, compared with their whole expansion, as to be incapable of producing any sensible deviation from the permanence of capacity.

In fusion or in vaporization, we discover a sudden change of capacity, because in these changes of state, there are sudden and complete changes in the arrangement of the particles. But, in expansion, there is no such sudden transition; it is gradual, and therefore it is only in a very considerable extent of it that any deviation will be perceptible.

There seems reason, therefore, to doubt of the permanence of capacities, or rather to suspect, that they may be different at different temperatures, probably becoming less as the temperature is low; and in different bodies these diversities may be various, as their relative forces of cohesion are different.

It has even been found, that, within temperatures which we can examine, this variation of capacity

from change of temperature, sometimes takes place. Gadolin observed it in linseed oil, and Crawford in some saline solutions, and in a mixture of sulphuric acid and water, and of alkohol and water; their capacities being increased by an augmentation of temperature. Crawford ascertained this, by finding, that when the constituent parts of these solutions or mixtures were mixed at a high temperature, they produced less sensible heat than when mixed at a low temperature; the compound, in the former case, being capable of containing more caloric than in the latter; and he confirmed this by direct experiment, mixing together equal parts of diluted sulphuric acid at different temperatures, when he found the resulting temperature greater than the arithmetical mean *. Now, if even in the small part of the scale of temperature at which we can make our experiments, there are, in some substances, perceptible deviations from this uniformity; much more is it probable, that in the whole extent of the scale, such deviations will happen, and to an extent of which we can know nothing. These variations arise probably from the expansion produced by caloric itself, by which the volume of the body is altered, and the law by which the quantity of caloric it contains at a given temperature modified. Now, we know absolutely nothing of the total amount of expansion in bodies from the real zero. The quantity of matter in a cubic inch of the densest substance, of gold, for example, may, if not acted on by caloric, oc-

* Treatise on Animal Heat, p. 479.

cupy a space inconceivably small; and therefore, if expansion enlarge capacity, as it probably does, it must be difficult or impossible to say what the amount of this enlargement is; of course, what may be the difference between the capacity of a body, estimated at the temperature at which we can subject it to experiment, and its capacity at much lower points in the thermometrical scale. If such variations do happen, they will probably be different in different bodies, and we have no means of knowing the law of variation which may be followed.

I must observe, however, that a different view of this subject has been given by Berthollet, and a cause pointed out, from which the quantity of caloric contained in bodies, in the first stage of temperature, may actually be greater than it will be higher in the scale. If caloric obey the usual laws of attraction, when it is in small quantity, relative to the body to which it is united, it will enter into more intimate combination, and hence the elasticity or expansive energy of it on which temperature depends may be overcome, and of course a larger quantity be required to produce a given temperature. From the peculiarity in the relations of caloric, it is not easy to determine how far this view is just; and, at any rate, it must be difficult or impossible to assign, even theoretically, how far these different causes will operate in modifying the quantities of caloric in bodies at different stages of temperature, or how far they may counteract each other.

From the operation of the general law now illustrated, with regard to the distribution of caloric in bodies, may be explained its extrication in many cases of chemical action, and its absorption in others. Dr Irvine first perceived its importance in this point of view, and that from it might be derived an explanation of the production of heat and cold from chemical mixtures. Having shewn the insufficiency of the vague hypotheses on which these phenomena had been attempted to be explained, particularly of the hypothesis of Newton, that the heat produced in the mutual action of bodies is owing to the violent motions and collisions of their particles, in consequence of the attraction by which they are combined, he observes, to use his own language, "that the reason why heat is produced by mixing fluids seems to be, that the ingredients which compose the mixed fluid are in a different state with regard to heat from what they were before: it would seem, that whatever is the cause of heat, it has a greater effect in heating the bodies after the mixture than it ought to have had in proportion to its power of heating the ingredients before mixture *." In other words, in such mixtures the capacity of the compound for caloric is inferior to the mean of the capacities of the substances combined, and hence an augmentation of its temperature from the caloric they contained, must take place. This luminous principle he illustrated, and likewise established by ex-

* Chemical Essays, p. 177.

periment. It was soon successfully applied by Dr Crawford to explain the heat which is produced in combustion, and other chemical processes, as well as the heat which is constantly generated in the system of animals, and which preserves them always at a temperature superior to that of the surrounding medium. On the other hand, when the capacity is enlarged, or that of the compound is greater than the mean capacity of its constituent parts, an absorption of caloric must follow, or the temperature be reduced; and on this principle is equally explained the cold attending some combinations, as the solutions of salts in water, and the intense colds generated by what are termed Freezing Mixtures. The general proposition is indeed probably just, that all variations of temperature, not arising from the immediate communication of caloric from an external source, originate in changes of capacity.

Sect. V. *Of the Quantities of Caloric which different forms of the same body contain.*

Having illustrated the law, that different bodies, at the same temperature, contain different quantities of caloric, in proportions regulated neither by their weights nor volumes, I have now to observe, that a similar law exists with regard to *different forms* of the same body; that a body in the fluid form contains more caloric, or requires a larger quantity to produce a given change of temperature in it, than it does while solid; and in the state of air or vapour, it con-

tains still more than it does in the fluid form. Hence, when a solid is melted, or a fluid is converted into vapour, quantities of caloric are absorbed, which have no effect in producing augmentation of temperature. Some philosophers have ascribed this phenomenon to a change of capacity; others have referred it to a different cause. It is necessary to state first the facts by which the general truth is established; the opinions with regard to it may then be considered.

The general fact of the absorption of caloric in these changes of form was discovered by Dr Black. Previous to the year 1762, he had described in his lectures some of the experiments by which it is demonstrated, and some years before that, the investigation appears to have occupied his mind. Wilcke, in 1772, read to the Academy of Sciences at Stockholm a dissertation, in which he states, as his own discovery, the fact that ice in melting absorbs a certain quantity of caloric; and there is no evidence that he was informed of the discoveries of Dr Black. The imperfect observations and crude conjectures of De Luc on the same subject can never be regarded as establishing any claim to the discovery; nor has it with more justice been assigned to Lavoisier, who, however, can scarcely be acquitted from the charge of having sought to appropriate it, by delivering many years afterwards the doctrine, with regard at least to aëriform fluids, with slight modifications, without mentioning Dr Black's name.

The truth of the general fact is sufficiently evident, when the phenomena attending liquefaction or vapo-

rization are attentively examined, and it was the observation of these phenomena that led Dr Black to the discovery. To take the illustration from the melting of ice, we observe, that its temperature may be considerably below 32°, and that if it be exposed to a warmer atmosphere, it will receive caloric, and gradually rise to that point of the thermometrical scale. But the moment it has reached it, the rise ceaſes; it begins to melt; melts slowly; and during the whole time of melting, its temperature, as well as that of the water flowing from it, are stationary at 32°. Yet caloric continues to be communicated to it as before; and that this caloric is absorbed by it, Dr Black remarked, is obvious, from the atmosphere being cooled by the melting ice, and a current of cold air descending from the vessel the whole time. Here, therefore, a quantity of caloric is absorbed, or disappears during the fusion.

The same phenomenon is observed when a fluid is converted into vapour. If we take a portion of water and communicate caloric to it, its temperature is raised, and this rise continues to proceed while the caloric is added, until, under the common atmospheric pressure, it arrives at 212° of Fahrenheit. At this point it begins to boil, or to be converted rapidly into vapour which escapes. But while it is suffering this change, its temperature is perfectly stationary, as is that also of the vapour arising from it, a thermometer in either indicating 212°. The conclusion is in this case the same as in the other. The vessel containing the water placed on a fire must con-

tinue to receive caloric after it boils as it did before; but the caloric thus added is absorbed without producing augmentation of temperature.

Dr Black not satisfied with the general observation of these phenomena, endeavoured to ascertain the fact with more accuracy, and to discover even the quantity of caloric which thus disappears.

In two glass vessels of the same size and weight, Dr Black put portions of water,—five ounces in each. The quantity in one of the vessels he froze by a freezing mixture, and removing the vessel into an atmosphere at 47°, allowed the ice in it to rise to the temperature of 32°. While this was doing, he cooled the water in the other vessel as low as possible without freezing any of it, or brought it to 33°, and placed in it a delicate thermometer. It was exposed to the same atmosphere at the temperature of 47° as the other, and the rise of its temperature observed by the thermometer. At the end of half an hour it had risen 7 degrees, or to the 40th of Fahrenheit's scale. The ice in the other vessel was not melted; its temperature remained at 32°, though it must have received caloric from the surrounding atmosphere equally with the other. It continued to melt slowly; at the end of 10½ hours a very small and spongy piece of it only remained unmelted at the surface of the water; in a few minutes more this was melted; and, on introducing a thermometer into the water, near the sides of the glass, its temperature was 40°; this rise, while in contact with the ice, being owing no doubt to its imperfect conducting power.

From this experiment, says Dr Black, it appears, that exposure to an atmosphere of 47° for 21 half hours was requisite to melt the five ounces of ice, and raise the temperature of the water produced from it to 40°. Now, the quantity of caloric which it had received during this time may be estimated from the quantity communicated to the water in the other vessel, and discovered in it by the rise of temperature it produced; for as the two vessels were exposed in situations perfectly alike, the same quantity of caloric must have been communicated to each. In half an hour, as much caloric had been communicated to the water as raised its temperature 7 degrees. In 21 half hours, therefore, the quantity of caloric communicated to the ice, and absorbed by it, must have been 7 + 21, or such as would have raised the temperature of the same weight of water 147 degrees. Yet no part of this appeared in the ice-water except 8 degrees, the temperature of that water at the end of the experiment being only 40°; the remaining 139 or 140 degrees must have been absorbed, therefore, by the ice in melting, without occasioning any rise in its temperature.

A quantity of ice, weighing 59½ drachms, at 32°, was put into a quantity of water, weighing 67½ drachms, at the temperature of 190 degrees. In a few seconds the ice was melted, and the temperature of the resulting fluid was 53°. In this experiment, the temperature of the water was reduced from 190° to 53°; the vessel in which this warm water was contained, and which must have been also at 190°, was likewise reduced to 53°; this vessel weighed 8 drachms; but

it being ascertained by experiment that its power in heating bodies is not more than half that of water, the 8 drachms may be regarded as equivalent to 4 of water, and as such may enter into the calculation. A quantity of water, therefore, weighing 67½ drachms, and a quantity of matter having the same heating power, amounting to 4 drachms, had their temperature reduced from 190° to 53°, or lost of caloric 137 degrees. These were communicated to the 59½ drachms of ice at 32°; and according to the relative proportions of the hot and cold matter, these, if there had been no loss, ought to have raised the ice 86 degrees, but they produced a rise of only 21 degrees. Here, therefore, 65 degrees disappeared,—a quantity which would have been sufficient to raise the temperature of a quantity of water equal in weight to the ice, 143 degrees. This quantity of caloric, however, had entirely disappeared, and so far, therefore, this experiment corresponds nearly with the former, in which 140 degrees had been lost. Dr Black confirmed both by a very simple experiment adding a given weight of ice at 32° to the same weight of water at 176°, when the ice was melted, and the temperature of the whole fluid was still not more than 32° *.

In the conversion of bodies from the fluid to the aëriform state, a similar absorption of caloric takes place, without raising the temperature either of the vapour or of the body suffering the change. This likewise Dr Black established by experiment.

* Black's Lectures, vol. i. p. 121—4, 5.

In several cylindrical tin-plate vessels, placed on an iron-plate, heated by a fire beneath, equal portions of water were put, at the temperature of 50°. After four minutes, the water began to boil, and in 20 minutes it had entirely boiled off. In four minutes, therefore, these portions of water had been raised from 50° to 212°, and of course had received a quantity of caloric capable of raising the temperature of that fluid 162 degrees, or at the rate of 40° $\frac{1}{2}$ each minute. After the ebullition commenced, caloric must still have been communicated from the hot iron-plate to the fluid as before; of course, in the 20 minutes, 810 degrees of caloric must have been absorbed. Yet these were not observable by any augmentation of temperature, the boiling fluid and the vapour arising from it being constantly at 212° *.

This result was confirmed by another experiment still more striking. A quantity of water was put into a strong phial, so as to fill it about one-half. It was corked strongly, placed in sand, and heat applied. It began to boil, but in a short time this ebullition ceased; the pressure on the water, from the accumulation of the vapour which had been formed being sufficient to prevent it; the fluid, therefore, had its temperature soon raised above 212°. While in this state, the cork was suddenly withdrawn. But instead of the whole water rushing out in vapour, as might have been perhaps expected, from its being heated above the temperature at which it passes into that state, only a small part of it escaped, and the remain-

* Black's Lectures, vol. i. p. 158.

ing quantity fell to the temperature of 212°; the quantity of vapour which was formed absorbing the whole excess of caloric above that point *.

The experiment was repeated by Mr Watt on a large scale. In a small copper digester with a valve, he heated a quantity of water, and when it began to boil, closing the valve, he allowed it to remain on the fire half an hour. Removing it, and opening the valve, a quantity of vapour rushed out with great force; but instead of the whole of the water having passed into vapour, at the very high temperature to which it must have been raised, he found, on opening the vessel, that of three inches of water, only one inch had escaped under this form †.

This experiment illustrates exceedingly well the phenomena attending the conversion of a fluid into vapour. Under the ordinary pressure of the atmosphere, water cannot be heated beyond 212°, since, as soon as it arrives at that point, vapour begins to be formed, and this absorbing a quantity of the caloric, prevents the temperature from rising, and in some measure conceals from us the real quantity of caloric received. But by thus confining it under a much greater pressure, we prevent the early formation of vapour, and when the pressure is removed, we see more clearly the quantity of caloric which the fluid absorbs, when it passes into the aëriform state, and which does not produce any augmentation of temperature.

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* Black's Lectures, vol. i. p. 159. † P. 160.

Dr Black remarked, that the same fact is established by the reduction of temperature which attends the transition of a body into vapour *in vacuo*. The temperature of hot water, for example, in the vacuum of the air-pump, will fall rapidly to the 90th, or even to the 70th degree of Fahrenheit. This is shewn still more remarkably in the evaporation of certain volatile fluids, as alkohol or ether,—a considerable degree of cold always attending it. This was first accurately observed by Dr Cullen. On wetting the bulb of a thermometer with either of these fluids, and suspending it in the air, he observed, that the mercury sunk rapidly. The more volatile the fluid was that was employed in the experiment, the greater was the reduction of temperature, and whatever hastened the evaporation, as directing a current of air on the wet bulb, increased the cold still more. By causing a rapid evaporation of the ether in the air-pump, such a degree of cold was even produced, as to freeze a portion of water in a vessel in which the phial containing the ether stood *. The explanation of these experiments is obvious. These fluids are so volatile as to evaporate at the common temperatures of the atmosphere; and in passing from the fluid to the aëriform state, they follow the general law, and absorb caloric from the matter with which they are immediately in contact.

Lastly, if a substance be disengaged from a combination, which, when it becomes free, passes into the

* Black's Lectures, vol. i. p. 162.

aëriform state, the chemical action by which it is disengaged, is attended with a much less production of heat than when a similar action is excited, but without the disengagement of an aëriform fluid, as was well shewn by Lavoisier, by several experiments *.

All these facts fully prove the truth of the general proposition, That when bodies pass from the solid to the fluid, or from the fluid to the aërial form, a quantity of caloric is absorbed, which has no effect in raising the temperature of the fluid, or of the vapour or air which is formed.

It may be expected, that the same quantity of caloric which is thus absorbed, will be again disengaged and rendered sensible, when the body returns to its former state. This accordingly happens. When a fluid, a quantity of water for example, is exposed to an atmosphere colder than what would be sufficient to freeze it, its temperature is gradually reduced, until it arrives at the point at which it congeals. But whenever it attains this, its temperature becomes stationary, and continues so until it has become entirely solid, although the colder atmosphere must have been abstracting caloric from it as before.

To render this more evident, Dr Black exposed a quantity of pure water, and another equal quantity of water to which a little salt had been added to prevent it from freezing, in similar vessels, to an atmosphere below 32°. Both of course were soon cooled down to the freezing point. The water in which the

* *Mémoires de l'Acad. des Sciences*, 1777, p. 430.

salt was dissolved continued to descend still lower in its temperature; but the pure water, beginning to freeze, remained stationary; the caloric which it had absorbed, when it passed from the state of ice to that of water, being now given out as it returned to the state of ice; and this caloric keeping its temperature stationary at 32°, though the cold atmosphere must have been acting on it in the same manner as on the other.

There is another experiment in which this evolution of caloric is rendered very apparent. Fahrenheit had observed, that if agitation be avoided, water can be reduced in temperature a number of degrees below its common freezing point, or 32°, without freezing. But if when it is cooled thus far, it be agitated, ice is instantly formed, and at the same moment the temperature rises to 32°. This arises from the evolution of the portion of latent caloric contained in the quantity of water that is frozen *; the quantity evolved being of course greater, as, from the previous greater cooling, more of the water is suddenly converted into ice.

A similar extrication of caloric attends the reduction of a vapour or a gas to the fluid form. If, for example, a certain weight of aqueous vapour be condensed, by receiving it in water, the water will have its temperature raised much higher, than by the addition of the same weight of water at the same temperature as that of the vapour. This was observed by Dr Black, and, with the assistance of Dr Irvine, he made

* Black's Lectures, vol. i. p. 128.

several experiments to discover the quantity of caloric thus evolved. It was difficult to guard against the abstraction of caloric, by the vessels and the surrounding air; but in general it was concluded, that the quantity evolved was not less than 774 degrees *. Mr Watt, in repeating the experiments, supposed it to be 825°, and from others he has fixed it at not less than 900°, and not more than 950 degrees of Fahrenheit's scale.

Mr Watt ascertained this too in another mode,—condensing the steam by strong mechanical pressure. He fitted a piston accurately to a metallic cylinder, and transmitting watery vapour through it, so as to expel completely the atmospheric air, when the cavity of the cylinder was filled with vapour, he pushed down the piston, so as suddenly to condense it, the caloric evolved, being communicated to water, in which the extremity of the cylinder had been put. The quantity of caloric thus extricated, according to Dr Crawford's statement, was such as would be sufficient to raise the temperature of an equal weight of a body having the same capacity as water, and which would not evaporate, 943 degrees of Fahrenheit's scale. Yet, previous to the condensation, the cylinder with the contained vapour, were only at the temperature of 212°.

Such are the facts and experiments by which Dr Black established the general truth, That when bodies pass from the solid to the fluid, or from the fluid to the aëriform state, they absorb a quantity of caloric which does not raise their temperature, and which is again

* Black's Lectures, p. 172.

evolved by them, when they return to their former state. The whole investigation is a model of physical research; the discovery, unlike so many others, was suggested by no prior train of speculation, but was separated, as has justly been observed, by a vast interval from the previous steps of our knowledge; and it was left in no respect imperfect, but was established by its author, on evidence which it is impossible to controvert, and to which the progress of the science has made no addition. To Dr Black is due the honour of having established the two principal laws yet known with regard to caloric,—that it is contained in bodies at the same temperature in specific quantities, and that it is absorbed, without producing augmentation of temperature, when bodies pass to the fluid or aëriform states,—laws which form the basis of much of the modern system of chemistry.

The portion of caloric, or according to the term then employed, of Heat, which is thus absorbed in fluidity or vaporization, Dr Black named Latent, to distinguish it from that which is discovered by the thermometer, and which, in opposition to the other, he termed Sensible. The term Latent, is convenient, as expressing briefly the portion of caloric absorbed or evolved in these changes of form, though there is probably no just foundation for distinguishing it as it exists in bodies, from the rest of the caloric which they contain.

In establishing the doctrine of latent heat, Dr Black's experiments were, in a great measure, confined to water in its different states. There could be no doubt, however, but that the same law is observed by other

bodies in their changes of form. This has been sufficiently ascertained by other chemists, and the quantities of caloric absorbed during these changes determined. Dr Irvine, who entered on this investigation at an early period, found, that spermaceti in melting, absorbed a quantity of caloric, which would be sufficient to raise the temperature of fluid spermaceti 145 degrees; wax, a quantity which would have raised its temperature when in the fluid state 175 degrees; and tin, a quantity equal to what would elevate its temperature when in the solid state 500 degrees. Wilcke states the quantity of caloric absorbed by ice in melting, as less than Dr Black gives. According to the average result of Dr Black's experiments, the quantity is equal to what would raise the temperature of water 140 degrees. Wilcke makes it equal only to 129°. Lavoisier and La Place fix it at the medium nearly, or 135° of Fahrenheit; while Gadolin makes it 143°. Landriani found by experiment, that sulphur, alum, borax, and some other salts, as well as some metallic compositions, when they pass into a solid state, from a state of fusion, obey the general law, and evolve a quantity of caloric, though he did not determine with any accuracy the quantities which were evolved *. Hassenfratz, assisted by some other French chemists, in freezing quicksilver ascertained, that in melting, it absorbs as much caloric as would raise the temperature of liquid mercury 152 degrees of Fahrenheit's scale †. Lastly, Mr Ir-

* *Journal de Physique*, t. xxvi. p. 88.

† *Journal Polytechnique*, t. i. p. 128.

vine has prosecuted his father's experiments, and determined the quantities of caloric absorbed in the liquefaction of the following bodies. In the liquefaction of bismuth, as much was absorbed as would have raised the temperature of the bismuth in its solid state 475° of Fahrenheit's scale; in that of tin 507°; of zinc 493°; of lead 150°; and of sulphur 143°. From these experiments we do not discover, as Mr Irvine has justly observed, "any ratio by which the quantity of caloric, absorbed in liquefaction, seems to be guided; it obviously does not increase with the difficulty of fusion, but most probably has some connection with the relative capacity of each body in its solid and fluid state *."

The following table exhibits the results of the experiments which have been made on this subject, the latent heat of each substance being measured, by the capacity of the solid, instead of by that of the fluid, which in the greater number of cases it is more difficult to determine; with the exception of the last article of the table, in which, from the difficulty of ascertaining the capacity of the solid, the latent heat is necessarily referred to that of the fluid. The basis of the table is taken from the Essay on Latent Heat, by Dr Irvine *jun.* already referred to.

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* Nicholson's Journal, vol. ix. p. 52.

	Melting point.	Latent heat.	Authority.
Ice,	32	155.5	Black.
——	——	150	Lavoisier.
——	——	143.3	Wilcke.
Spermaceti,	113	145	Irvine.
Bees wax,	142	175	——
Tin,	442	500	——
Bismuth,	476	550	——
Lead,	594	162	——
Zinc,	700	493	——
Sulphur,	226	143.6	——
Quicksilver	— 40	152	Hassenfratz.

From this absorption of caloric, which takes place when bodies pass from the solid to the fluid, or from the fluid to the aëriform state, many chemical and natural phenomena may be explained.

The absorption of caloric, accompanying the change from the solid to the fluid form, explains the fixity of the point in the thermometrical scale at which bodies melt. Ice, for example, melts at 32° of Fahrenheit, and whenever any mass of ice is heated to that temperature, the farther addition of caloric, however rapid, has no effect in raising its temperature, till the whole mass is converted into water; since, as quickly as the ice is melted by the caloric, as quickly is a large portion of it absorbed by the fluid formed. This is exemplified in the long time before large masses of ice, or collections of snow, are melted by a thaw. Were it not for this absorption of caloric, the thawing of immense masses of ice and snow, in the colder climates, at the approach of spring, would take place almost in-

stantaneously, whenever the atmosphere arrived at the temperature of 33° ; whereas, from this circumstance, the melting is gradual and progressive, by which the water that is formed is distributed more slowly, and, at the same time, the too sudden rise of temperature, which in such climates would prove fatal to vegetables, is prevented.

The reverse of this, or the extrication of caloric, which takes place when water is converted into ice, is equally beneficial; since, were it otherwise, the freezing of large collections of water would be extremely rapid, whenever the temperature of the atmosphere was at or below 32°. But from this extrication, the freezing is very gradual, and, at the same time, a large quantity of caloric is given out by the water in passing to the solid state, by which the approaching cold is moderated, and the congelation rendered more slow.

The same observations may be made with regard to vaporization. When the earth is much heated by the sun's rays, a very large quantity of water is evaporated from its surface, and from rivers and the ocean, and the conversion of this quantity of water into vapour, is necessarily accompanied with the absorption of a large quantity of caloric. Hence evaporation is the most powerful agent employed by nature to moderate excessive heat. On the contrary, when the vapour of the atmosphere is condensed by cold, and descends in the form of rain or snow, it gives out the caloric it had received, which is then beneficial rather than hurtful.

The process of artificial refrigeration is explained on the same principle. By allowing water to filtrate

slowly through porous earthen vessels, so as to present an extensive humid surface to the atmosphere, it passes rapidly into vapour, and in this vaporization absorbs so much caloric as to produce a considerable degree of cold. Liquors are cooled, and in warm climates ice formed, by arrangements of this kind, and this even when the temperature of the atmosphere is above 32° *.

The theory of freezing mixtures, is likewise deduced from the doctrine of latent caloric. These are mixtures of saline matters, which, at the common temperature, by their mutual chemical action, pass rapidly into the fluid form, or are capable of being rapidly dissolved in water, and by this quick transition to fluidity, absorb caloric from the surrounding matter, and produce degrees of cold, more or less intense.

In other cases of chemical action, substances pass from the gaseous to the fluid, or from the fluid to the solid form, and the rise of temperature which attends these transitions, may be referred to the evolution of latent caloric, which must be their result.

The use of steam, which has been introduced as a vehicle and source of heat, affords an example of the scientific application of these principles. By conveying steam into water, it is condensed, and by the evolution of the latent caloric by the condensation, the temperature of the water is raised, so as soon to arrive at 212°. In certain arts, as in that of dyeing, where large quantities of water are to be heated in separate vessels, this method has superior advantages. By having a common boiler, from which the vapour

* Philosophical Transactions, 1793, p. 56.

is conveyed by tubes, the loss of heat is much less than if fire was applied to each vessel, and at the same time the vessels are subject to less wear, and may be constructed at less expence. This method has accordingly been employed with success. Another application of the same principles is that of heating rooms by conveying steam through tubes, proposed in an early volume of the Philosophical Transactions, and since revived. The steam in its progress is condensed gradually, and gives out its latent caloric, so as to produce an equable warmth. Count Rumford has also proposed, that this method of applying heat should be used in the drying of gunpowder, as not attended with that risk which must be incident to other methods.

The modern improvements in the steam-engine, as they originated from Dr Black's discovery, so they afford a very striking exemplification of the doctrine of latent caloric. In the engine wrought previous to the improvements of Mr Watt, the steam was received into a cylinder, to which a piston was adapted; the piston by the weight attached to its arm being elevated to the top of the cylinder, and the cavity beneath filled with steam. This was condensed by a jet of cold water, when the piston was of course immediately forced down by the pressure of the atmosphere. To counterbalance this, steam was again introduced from beneath, and thus the alternate elevation and depression of the piston were effected. But in this way, it is obvious, that there was an immense waste of heat, and this altogether concealed,

while the facts relating to latent caloric were unknown. By the jet of cold water not only is the steam condensed, but the cylinder is likewise cooled, as is also the piston in its descent. When, therefore, the steam from beneath is again introduced, a great part of it must be condensed and lost, by its caloric being abstracted by the cold cylinder and piston, and its elasticity cannot operate with effect until the whole is again elevated to 212°. At each stroke of the engine this waste is repeated, and thus, according to Mr Watt's calculation, at least half of the steam produced in the boiler is lost.

Mr Watt's principal improvements consisted, 1st, in condensing the steam, not in the cylinder, but in another vessel communicating with it by a pipe with a valve or stop-cock, which being exhausted of air, the steam rushed into it whenever the communication was opened, and was condensed by the vessel being kept always cold by immersion in water; and, 2dly, by excluding from the cylinder the atmospheric air, by which it would be cooled, and depressing the piston by steam introduced above it, and condensed in the condensing vessel alternately with the steam beneath. Thus, the whole may be kept at the temperature of 212°, and the immense waste of heat in the old method entirely obviated. Dr Black justly characterises the engine in this state as the master-piece of human skill, and no less justly observes, that it has not been "the production of a chance observation, but "the result of deep thought and reflection, and really "a present by philosophy to the arts."

Having stated the phenomena and the applications of latent caloric, it remains only to consider the opinions that have been advanced with regard to its cause. It has been considered under very different points of view; some philosophers having supposed the absorption of caloric that attends liquefaction and vaporization to be the cause of these changes, others regarding it only as the effect.

By Dr Black the first of these opinions was maintained. The immediate cause of fluidity he supposed to be a certain quantity of heat or caloric, which is absorbed by the body when its temperature is raised to a certain point, which remains concealed in it, and which continues in this state without suffering any increase or diminution, while the body continues fluid, but which, when it passes to the solid state, is again disengaged, and rendered sensible. "I consider," says he, "fluidity as depending immediately and inseparably on a certain quantity of the matter of heat which is combined with the fluid body in a particular manner, so as not to be communicable to a thermometer or to other bodies, but capable of being extricated again by other methods, and of re-assuming the form of moveable or communicable heat *." He applied the same theory to vaporization. "When a fluid body is raised to its boiling temperature by the continual and copious application of heat, its particles suddenly attract to themselves a great quantity of heat, and by this combi-

* Black's Lectures, vol. i. p. 144.

" nation their mutual relation is so changed that they " no longer attract each other, but avoid each other, " separating to at least ten times their former dis- " tance, and would separate much farther were they " not compressed by the weight of the atmosphere; " and in short, they now compose a fluid, elastic and " expansive like air. This new form of aggregation " is the effect of a new combination of heat with the " primary particles of water, and is a sufficient indi- " cation of this union, in the same manner as fluidity " was a sufficient mark of a sudden and copious com- " bination of heat with the particles of ice *."

In this theory, then, the absorption of caloric in liquefaction and vaporization is considered as the cause of these changes of form. Dr Black, though he did not state the opinion fully, appears to have been inclined to suppose these changes analogous to chemical combination, to regard the caloric which disappears as entering into union with the body fused or evaporated, and owing to this combination its loss of properties. He considered, says Professor Robison, latent heat " as *united* with " the substance of the body in a way very much resem- " bling many chemical combinations." And, again, " he considered heat as the active cause, both of fluidity " and of vapour, producing those new modes of aggre- " gation by a true chemical combination with the par- " ticles of the body †." This opinion has been more

* Black's Lectures, vol. i. p. 175.

† Ibid. vol. i. p. 514.

fully developed, and expressed with less hesitation by other chemists, as by De Luc * and Seguin †.

Dr Irvine viewed these phenomena under a very different light. He saw, that if the body in its liquid state had a greater capacity for caloric than while solid, a quantity of caloric must be absorbed during its liquefaction, which will have no effect in raising its temperature. And to this principle he was disposed to refer the phenomena of latent heat. The changes of form from the solid to the liquid, and from the liquid to the aëriform state, in any body, he supposed to be accompanied with augmentation of capacity; probably from a change in the positions of the particles; from this a quantity of caloric must be absorbed, proportioned to this augmentation, which can occasion no augmentation of temperature; and when the body is reduced to its former state, its capacity for caloric being diminished, it must give out that portion which it had absorbed. In either case, therefore, the temperature must continue stationary while the change is going on; or while the body is melting, a quantity of caloric must be absorbed to satisfy the increased capacity; and while it is becoming solid this caloric must be given out. Nor does the caloric thus absorbed by the fluid or vapour exist in it in any other mode than the rest of the caloric it contains; but the body in these states merely requires more caloric to produce a certain temperature than it does while solid; and the evolution or absorption of ca-

* *Idées sur la Meteorologie.*

† *Annales de Chimie*, t. iii. p. 193.

loric is only the consequence, not the cause of the change of form.

This view of the subject is thus stated by Dr Irvine. "The reason why a body cannot be heated while it is melting is, that it is then changing its capacity. From a substance that was easily heated, it changes to one that is heated with difficulty. All bodies in a fluid state seem to be heated with more difficulty than when in a solid state. Not that a body in a fluid state transmits heat more slowly than when the same body is in a solid state. On the contrary, it transmits heat better in a fluid than in a solid state. But the same quantity of heat applied to the same body in a solid form, and in a fluid state, will heat the solid a greater number of degrees than it will the fluid *."

Reserving the more full consideration of this interesting, but rather abstruse and complicated subject to a note, it is sufficient for me to remark in this place, that the theory of Irvine affords an adequate explanation of the phenomena, and that its first principle is established by experiment. The latter subject engaged much the attention of Dr Irvine, and he made a number of experiments, for many succeeding years, to ascertain the fact. To do so with accuracy was extremely difficult; as, in comparing the capacity of a body in the solid and in the fluid state, it was necessary that in the progress of the experiment it should not change its form; that in determining its capacity in the solid state it should remain solid; and in determining it in the fluid form it should con-

* Irvine's Essays, p. 52.

tinue fluid. By employing the medium of a third substance, quicksilver, iron-filings, river-sand, or pounded glass, he endeavoured to discover the relative capacities of ice and water, operating on the ice when the temperature of the atmosphere was considerably below 32°, and on water at temperatures of the air above 32° of Fahrenheit. The result always was, that the capacity of water is greater than that of ice; and in a ratio, as he found reason to believe, not greater than 10 to 8. "He extended his theory to "all other bodies, and in some cases determined, and "in all inferred, that it is a general law of nature "that the capacity of all solids for heat is increased "by fusion, and that of all fluids by vaporization *." Magellan states the respective capacities of water and ice to be as 10 to 9; and Dr Crawford found that the capacity of watery vapour is greater than that of water, in the proportion of 115 to 100. The principle of the theory is therefore established.

That it affords a satisfactory explanation of the phenomena, may likewise be shewn. No proposition can be more undeniable, than that if the capacity of a body be enlarged, there must either be a sudden fall of temperature, if caloric be not communicated from an external source, to keep it up, or if such a communication be made, a quantity of caloric must be absorbed by the body, without having any effect in raising its temperature. The temperature of bodies depends partly on their capacities, and partly on the

* Essays, p. 56.

quantity of caloric applied to them; and although this quantity be increased, if the capacity is at the same time proportionally augmented, no change of temperature can take place. Since, therefore, the capacity becomes greater when ice passes to the state of water, and that of water suffers another augmentation when it passes to the state of vapour, the phenomenon that does occur must necessarily happen—an absorption of caloric without any rise of temperature. The quantity which is absorbed will be in proportion to the capacity of the body in the new form, or it will require as much caloric as is requisite to keep up its temperature according to that capacity, from the point of privation in the thermometrical scale to the point at which it has assumed the new form; and we know of no fact which shews that the quantity really absorbed is not in proportion to this.

It may be said, that we are not certain that the augmentation of capacity is proportional to the quantity of caloric absorbed, and that besides the portion which the augmented capacity demands, another quantity may enter into chemical union. This, indeed, cannot be ascertained by direct experiment, for we have not discovered with certainty the absolute quantity of caloric contained in bodies, from whence only we could discover whether the quantity absorbed in these changes of form corresponds with the changes of capacity. But if the opposite hypothesis is to be left to this bare possibility, it cannot be said to have much support; and the maxim in philosophy, That causes are not to be multiplied to account for phenomena,

precludes the admission of a *supposition* unsupported and unnecessary.

The other theory, that which considers the change of form as produced by an intimate combination of the caloric which disappears with the body whose form is altered, rests on a principle entirely hypothetical. It is less simple and comprehensive, and derives support from a limited view of the phenomena. —Note B.

Sect. V. *Of the Absolute Quantity of Caloric in Bodies.*

Caloric, whatever may be its nature, must be contained in bodies in limited quantity. It may therefore be proposed as a problem, What the absolute quantity is; or at what distance in the thermometrical scale, from a given temperature, would the point at which bodies would be entirely deprived of caloric, be found? The farther we reduce the temperature of a body, the nearer we approach this point; and could we actually arrive at it, it is evident that by commencing from it the thermometrical scale, we should ascertain the quantity of caloric which a body contains, and the degrees on that scale would then be an exact measure of the absolute quantity of caloric existing in any body at a given temperature.

We can never, however, expect, by any actual reduction of temperature, to abstract from bodies all the caloric they contain. Still though this be impracti-

cable, it has been attempted to discover by calculation, at what distance in the thermometrical scale this point of absolute privation, or the real zero, as it has been termed, would be placed; and I am to state in this section the methods which have been employed, and their results.

The possibility of solving this problem seems first to have occurred to Dr Irvine, and to have been suggested to him from the consideration of the change of capacity which attends liquefaction, combined with the quantity of caloric which is absorbed. It is obvious, that if the quantity of caloric contained in bodies be proportioned to their capacity, from knowing that capacity in the different states in which a body exists, and the quantity of caloric which it absorbs or gives out when it suffers a change of form, the extent of which experiment can discover to us, we have the data from which the whole quantity of caloric existing in it may be discovered; that quantity bearing a certain relation which the difference of the capacity of the body in its two states discovers, to the quantity absorbed or given out in the change of form. Thus, suppose the capacity of water to be to that of ice as 10 to 9, water, at the same temperature with ice, that is at 32°, at which both may exist, will consequently contain one-tenth more caloric in equal weights. When water, therefore, is converted into ice, it must give out this tenth part, and by ascertaining what the amount of this is, we discover what the quantity of caloric is which water contains, or what quantity, numbered by degrees of temperature, will be requisite to raise it from the

real zero to 32°. The quantity evolved has been stated by Lavoisier at 135°, by Dr Black at 140°, by Gadolin at 143°. Supposing the number approaching nearest to the medium of these, 140°, be taken, this, according to the preceding statement, is the 10th part of the caloric which water at 32° contains; of course, to obtain the whole quantity, this portion is to be multiplied by 10, which gives 1400 as the whole caloric in water at 32°; or 1260 degrees, such as those contained in the water, now remain in the ice. But the capacity of this ice being one-tenth less than that of water, the quantity of caloric which would raise the temperature of water 1260° will raise that of ice 1400°. Hence either water or ice at 32° contains a quantity of caloric capable of raising its own temperature 1400 degrees, and of course the zero is at that distance, measuring, by the divisions of Fahrenheit's scale, from 32° *.

On these principles is founded the theorem which

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* It is proper to state, that Dr Irvine placed the zero at about 900° below 0 of Fahrenheit, from finding as the result of his experiments, a different proportion between the capacities of water and ice. Instead of being as 10 to 9, he found it to be nearly as 10 to 8; and as Dr Irvine appears to have made the experiment to ascertain these comparative capacities with more care than any other person, his estimate would be perhaps to be preferred, if, as I shall soon have to state, the discordant results on this question did not render all the numbers that have been given doubtful.

Dr Irvine gave for calculating the real zero. Without employing algebraical terms, it may be thus stated. The capacities of the solid and fluid being as the whole quantities of caloric they contain, it will follow that the difference between the numbers which express their capacities, is to the number which expresses the capacity of the fluid, as the difference between the quantities of heat which each contains, measured according to the capacity of the fluid, is to the number of degrees which will express the quantity of caloric it contains from zero. The following general formula, therefore, may be given for the calculation. Multiply the number which expresses the quantity of caloric absorbed when the body passes from the solid to the liquid, or given out when it passes from the liquid to the solid state, by the number denoting the capacity of the fluid. Divide the product by the number which expresses the difference in the capacities of the body in its two forms; the quotient will be the number of degrees of temperature between the freezing point of the fluid and zero, measured according to the capacity of the fluid. Or, if we take as the multiplicator, the number which expresses the capacity of the solid, the quotient of the division will give the quantity of caloric contained in the solid at its melting point, measured by degrees according also to the capacity of the fluid. And, to bring these to degrees, measured by the capacity of the solid itself, it is only necessary to add the number of degrees absorbed in its transition to the fluid form.

All bodies which have a common temperature,

must be at the same distance from the commencement of the thermometrical scale. It is no doubt true, that they contain, at the same temperature, very different quantities of caloric; but this arises from the difference in their capacities, or from their requiring different quantities to produce the same augmentations of temperature. The degrees of temperature are the same, though the quantities requisite to produce these degrees be different. If, therefore, water at 32° be distant from the real zero 1400 degrees, all other bodies must be distant from it the same number of degrees; the number in each being measured by degrees, according to its own capacity *. Hence, if

* If this circumstance, the reckoning the degrees according to the capacity of the body referred to, be not attended to, the results cannot correspond; and there is reason to believe that this has sometimes been overlooked. Thus, some authors, from the calculation in the text, founded on the capacities of ice and water, have stated the zero at 1260° below 32°. The caloric contained in ice at 32°, is no doubt according to the data on which that calculation is founded equal to 1260°, measured by the capacity of water; but these ought to be measured by the capacity of the ice itself; and as this is one-tenth less than that of water, this will bring them equal to 1400°. In like manner, the quantity of caloric in water at 32°, according to the same data, will be equal to 1400° above zero; these degrees being measured by the capacity of water. And, in all cases, the distance at which any body, at a given temperature, is from zero, ought to be stated in degrees measured by its own capacity; and if this be done, the distance of that

this point be truly determined, it must turn out the same when determined by other methods on other bodies. And this agreement, if obtained, will be a proof of the justness of the principles on which the solution of the problem has been attempted.

Dr Crawford endeavoured to determine it by a calculation, founded on the capacities of the two simple

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point from a given temperature will in all turn out the same, though the real quantities of caloric they may contain will be different. This will be found illustrated by a diagram, in a Note, at the end of the volume. For the following general formula, for calculating the zero, applicable to the measurement by the capacity either of the fluid or of the solid, and more comprehensive than any I have met with, I am indebted to my friend Mr Jackson of Ayr. "Let C & c represent the capacities of the fluid and the solid respectively; H & h their absolute quantities of heat, as measured by thermometrical degrees, according to the capacity of the fluid; H′ & h', the same as measured according to the capacity of the solid:

Then $C : c = H : h$

$$\& \; C-c : C = H-h : H = \frac{(H-h)\,C}{C-c}$$

Also $C : c = H' : h'$

$$\& \; C-c : c = H'-h' : h' = \frac{(H'-h')\,c}{C-c}$$

Or, as the difference of the numbers expressing the capacities of the fluid and the solid, is to the capacity of either; so is the difference of their absolute quantities of heat, at the point of liquefaction estimated according to the scale of that capacity, to the distance on the same scale between the point of liquefaction and the absolute zero."

substances which, by their combination, form water, the quantity of caloric which is extricated during their combination, and the capacity of the product. It is evident, that supposing the specific calorics of the elements of water to be the same as their absolute calorics, by knowing these specific calorics, the quantity of caloric which is given out during their combination, and the specific caloric of the substance they form, we may discover the absolute quantities they contained, or, measured by their capacities, the number of degrees at which they are distant from the zero. Dr Crawford calculated this to be 1550°, from 50° of Fahrenheit, or placed the zero at 1532° below the freezing point of water *.

Gadolin instituted a series of experiments on this subject, which appear to have been executed with much care †. He ascertained the capacity of sea-salt, and the capacity of the solutions it forms with given quantities of water, and observed the degrees of cold which were produced in dissolving the salt in the various proportions of water; and from these it appears, that the point of privation is 1400 degrees below 0 of Fahrenheit, or 1432° below the freezing point of water. And other experiments made on the cold, produced in the mutual action of snow and salt, and on the heat excited by the combination of sulphuric acid with water, coincided with this more closely than from the delicacy of the experiments could have been expected. They appear to be by far the most com-

* Treatise on Animal Heat, p. 267. † Ibid. p. 457.

plete and accurate series of experiments which we yet have on this subject.

But I have now to state, that the experiments of Lavoisier and La Place with the calorimeter, give results altogether inconsistent with these, and with each other. From mixing at the temperature of melting ice, water and quicklime in the proportion of 9 to 16, discovering by the calorimeter the quantity of caloric given out, and comparing this with the capacities of the lime, the water, and the mixture of the lime and water, the quantity of caloric contained in the water at that temperature, or, in the equation they employed, x, was found $=1537.8$ degrees, according to Reaumur's scale, or 3460° according to Fahrenheit's; in other words, water at its freezing point, contains, according to the calculation founded on this experiment, 3460 times more caloric than what elevates its temperature one degree of Fahrenheit's scale, and of course the zero is that number of degrees below 32°. An experiment, conducted in a similar manner, on the heat evolved by a mixture of sulphuric acid and water, compared with the capacities of the substances before and after mixture, gave $x=3241.9$° R., or 7294° F. A third experiment, in which the acid and water were mixed in other proportions, gave $x=1169.1$° R., or 2630° F. And lastly, from the mixture of nitric acid and quicklime, in the proportion of $9\frac{1}{5}$ to 1, the result, as La Place states it, was $x=\frac{1889}{-0,01783}$, a value, as he remarks, "physically impossible, and consequently proving the falseness of

the hypotheses calculated on, if the specific calorics employed in the calculation were rigorously exact *."

This conclusion, taking into account this condition, no doubt follows both from the result of the last experiment, and likewise from the discordant results of the others. "But it ought to be observed," adds La Place, "that a very trivial alteration, at most a fortieth, in the estimation of the specific calorics of the substances employed, will be sufficient to establish a correspondence between all our results;" for the quantities of caloric given out in these combinations, bearing so inconsiderable a proportion to the absolute caloric, a slight alteration in the estimation of the capacity will have a very important effect in the calculation from which the zero is deduced; "nor can we affirm," he continues, "that an error so trivial has not crept into our experiments, and therefore they are neither favourable nor adverse to the theory; and all that can be concluded, is, that if the theory on which this calculation is established be just, the absolute heat of bodies the temperature of which is that of melting ice, must be at least 600 degrees of Reaumur's scale, (1350° of Fahrenheit's); for to make it a number below 600°, it is necessary to suppose, in our experiments, errors greater than those of which they appear to be susceptible *."

With such an admission, and considering, that in no case whatever can we be assured that the capacity of a body is ascertained with accuracy, so as to preclude the error of a fortieth part, and that, with regard to many substances, the results of different experiments are

* *Mémoires de l'Acad. des Sciences*, 1780, p. 386.

much more discordant than this, there can be no hesitation in drawing the conclusion, that the experiments of Lavoisier and La Place do not invalidate the theorem of Irvine. Of all, indeed, that have been made on this subject, they appear entitled to the least confidence. They are related in a loose manner; and the unavoidable errors to which the calorimeter, (the instrument by which both the capacities and the quantities of heat evolved were ascertained), is liable, must establish the candid admission of La Place, so much in contrast with the hasty conclusions of Seguin on the same subject, that errors sufficient to give rise to these discordant results had been present.

In addition to these experiments, Seguin has calculated at what point the zero would be placed, from various experiments by Lavoisier, on the caloric rendered sensible during the burning of different combustible bodies. From the heat produced in the burning of phosphorus, he placed it at 1894° below the freezing point of water,—from that produced in the burning of hydrogen at 1663°, and from that evolved in the combustion of charcoal at 2709° *. It is evident, that these numbers do not differ so much as the preceding; and although they are drawn from experiments, in which a greater proportion of the absolute caloric must have been evolved, yet still the same correction, or one not much greater, would reconcile them; and when we consider the difficulties attending the estimation of the capacities of aërial bodies, there is every reason to believe, that errors not less important enter into the cal-

* *Annales de Chimie*, t. v.

culations from these experiments, than in those from the experiments of Lavoisier and La Place.

From the preceding statement, it appears that the greater number of experiments which have been made on this subject, and especially those in which the sources of error were least considerable, those of Irvine, Crawford and Gadolin, agree in placing the real zero at a point between 1200 and 1500 degrees below the freezing temperature of water; and even in the experiments which differ most widely from this, those of Lavoisier and La Place, it is admitted by their authors, that errors to which they acknowledge their method liable, may have given rise to the discordant results, and that admissible allowances for such errors may reconcile them with the other experiments. On a subject in which it is so difficult to obtain a perfect precision, this general agreement,—an agreement, too, obtained in various modes of experimenting, it must be acknowledged, affords presumption of the truth of the principles on which the calculation is founded. At the same time, the other discordant results, prove the errors to which the attempt to reduce the theorem to practice is liable, and prevent us from placing all the confidence we otherwise should do in any solution of the problem which has been given; though without in the least invalidating the theory on which it has been attempted. If the capacities of bodies shall ever be determined with perfect accuracy, the question will assume a different form,—the place of the real zero will either be determined with certainty, or the falsity of the theory be demonstrated. At present we can expect neither. If we examine the table

of capacities, we find such differences in the numbers affixed to the same substances by different experimenters, as sufficiently prove the difficulty of fixing them with such accuracy, as to admit of either conclusion.

The investigation of this problem is however rather a subject of curiosity than of utility; and it is far from being what Professor Robison states it, that which "gives the chief importance to the whole doctrine of specific heats." The importance of that doctrine consists in its giving the theory by which we account for the variations of temperature from chemical action, our knowledge of the relations between the specific caloncs of different substances, enabling us to do so with perfect accuracy, at that part of the scale of temperature at which they take place, though we know nothing of the absolute quantitie of caloric they contain. Note B.

From the diversity of opinions which have prevailed among chemists respecting the states in which caloric exists in bodies, several forms of expression have been introduced, which may, without impropriety, be explained in this place.

Free Caloric is caloric in that state in which it expands bodies, and, accumulated to a certain extent, produces the sensation of heat. It is synonymous with the *sensible heat* of Dr Black, and with the *caloric of temperature* of some other chemists.

The *Specific Caloric* of the French chemists expresses the relative quantities of caloric contained in equal weights of different bodies at the same temperature, or the quantity of caloric peculiar to any body. Thus we say that the specific caloric of water is to that of mer-

cury as 28 to 1. The term is synonymous with the *Comparative Heat* of Dr Crawford. Others have used the phrase *Relative Heat* in a similar sense. Wilcke, however, employs this term Relative Heat to denote the specific caloric of a body when estimated, not by the weight, but by the volume.

The disposition or property by which bodies contain certain quanties of caloric at any temperature, is termed their *capacity for containing caloric*. The term is generally used in a comparative sense; as when the capacity of any body, that of mercury, for example, is said to be so much, compared with that of another, of water for instance. Hence the phrase can generally be substituted for that of specific caloric, the cause being thus placed for its effect. The specific caloric is the quantity contained in any body, the capacity the property by which that quantity is contained, and hence they must be proportional to each other.

Latent Caloric, or Latent Heat, is the expression used to denote that quantity of caloric which a body absorbs when it changes its form. The expression is perhaps unnecessary, the quantity of caloric which the body contains in its new state being properly specific caloric.

Combined Caloric is that portion of caloric supposed to be contained in any body chemically combined. I have already observed, that it is very doubtful whether caloric exists in such a state.

The *Absolute Heat* of Dr Crawford denotes the whole quantity of caloric which any body contains. It is expressed according to the language of the new nomenclature by saying the absolute quantities of caloric contained in bodies.

Sect. VI. *Of the Nature of Caloric.*

The nature of that power which we denominate Heat, has long been a subject of discussion, and the question with regard to it is not yet unequivocally determined; for although the greater number of modern chemists have inclined to the opinion that it is a peculiar subtle matter, some have maintained the hypothesis that the phenomena which it exhibits do not depend on a material agent, but arise merely from a vibration of the particles of matter. This hypothesis appears to have originated with Lord Bacon. He first investigated this difficult subject; and finding, from a copious induction of facts, that the causes which give rise to increased temperature, and all its effects, are in general such as excite motion among the particles of bodies, and that causes producing such motion are as generally followed by rise of temperature, he concluded, that "heat arises from violent motion in the internal parts of bodies." In pointing out the nature of this motion, he adds, that it is an expansive one, tending to dilate the body in which it happens; its tendency is also to rise upwards; that though the smaller particles dilate themselves, this motion is restrained, so that it becomes constantly alternating, or *vibration* performed with rapidity among the minute particles;—in his own words, "Calor est motus expansivus, cohibitus et nitens per partes minores *."

This notion, with regard to the nature of caloric, was adopted by Boyle and by Newton, and at a later period by Macquer among the French chemists.

* Works of Lord Bacon, vol. iv. p. 328.

The other opinion, however, continued to be more generally embraced. It considers caloric, or the power by which expansion and change of form are produced, as a subtle elastic fluid diffused over matter, with which all bodies are more or less penetrated, and which produces in them these peculiar effects. This opinion was maintained by Homberg, Lemery, Boerhaave, and the greater number of chemists, and though confessedly hypothetical, it seemed so probable, and explained the phenomena so satisfactorily, that it at length came to be generally received. It was admitted, though with some reserve, into the antiphlogistic system, and by many chemists was even considered as nearly a demonstrated truth.

Of late, however, its justness has again been called in question, and the doctrine of Bacon revived; and it will be necessary to review the arguments by which these different opinions are supported.

In favour of the existence of caloric as matter, little could formerly be stated, except that such a supposition accords with the phenomena of temperature, its various changes, and the effects these produce upon bodies with respect to expansion and change of form. If a body is increased in volume, the natural conclusion is, that some other matter, some subtle fluid has been introduced into its pores by which it has been expanded, and the accumulation of this fluid, by augmenting the expansion, will at length set the particles to such distances as to produce the fluid or aëriform state. Since temperature can be communicated from one body to another; it is natural to refer the distribution to the communication of this subtle matter; and if different

bodies have their temperatures unequally raised by equal communications of this power, the phenomenon may be explained by the supposition of difference in density, or of affinity between the power itself and the matter to which it has been communicated. So far the effects produced by caloric—its passage from one body to another, and its relations to matter in general, are satisfactorily explained on the supposition that it is a peculiar fluid, the particles of which are mutually repellent.

It has been objected indeed, that in explaining expansion, and other effects of caloric, on the supposition of a fluid endowed with a repulsive power, the difficulty is only removed one step back, since we have still to explain the cause of the elasticity of this fluid. The objection is so far just; but it is to be observed, that the phenomena admit of a better explanation from the supposition of the existence of such an elastic fluid, than they do from the mere direct assumption that the property of repulsion may be an attribute of matter in general in peculiar states, since on the former supposition we can easily explain the communication of the phenomena of heat from one body to another, while on the latter we do not perceive how, by the contact of two bodies at different temperatures, the repulsive power of the one should be increased, and that of the other diminished.

There is one phenomenon, however, the explanation of which is not so obvious, and which, since it has been accurately investigated, has afforded, in the opinion of many, sufficient reason to doubt of the materiality of caloric. It is the production of increased temperature by friction or percussion. Examples of this are very

familiar. If a rod of iron be beat upon an anvil, it soon becomes hot, and if the beating be continued, its temperature rises to ignition. A rope rapidly revolved round any solid body will, in like manner, be soon so much heated, that it will catch fire; or the friction of two pieces of hard wood against each other will heat them so much as to kindle them. The spark struck from a flint and steel is another example of the same kind.

In these instances it was supposed that the caloric contained in the bodies was expelled by the repeated impulse arising from the friction or percussion, forcing the particles nearer to each other. Some modern chemists, however, in consequence of having determined with more accuracy the quantity of caloric disengaged by these operations, and the circumstances connected with its production, have endeavoured to shew that this explanation is insufficient, and have adopted the opinion of Bacon on the nature of caloric.

Count Rumford had observed, that in the boring of cannon, by the friction of the borer a very large quantity of caloric is rendered sensible. To ascertain its quantity he fixed a solid cylinder of brass in a trough filled with water, and having adapted the borer to it connected with the machinery by which it is turned, it was made to revolve in the usual manner, at the rate of 32 times in a minute. Heat was soon excited, and of course raised the temperature of the metal, and of the surrounding water. In an hour the temperature had risen from 60° to 107°, and in two hours and a half the water was brought to boil, the quantity of this water being 18 lbs.; the apparatus itself, which was of course raised to the same temperature, weighed 15 lbs.

In investigating the source of this caloric, Rumford endeavours to shew that its extrication could not arise from a diminution of capacity, since the capacity of the borings of the metal, he found by experiment to be the same as that of the solid metal. The circumstances of the experiment proved, that the atmospheric air has no share in the production of the heat, since its access was prevented by the water surrounding the apparatus; neither does the water appear to have contributed to it by any chemical agency, since it underwent no change; and lastly, the caloric, he thinks, could not have been communicated by the surrounding bodies, since they were in fact receiving it from the matter subjected to friction. He concludes, and apparently with justice, that any thing which any insulated body or system of bodies can furnish without limitation, "cannot possibly be a material substance;" and it appears to me, he adds, "to be extremely difficult, if not quite impossible, to form any distinct idea of any thing capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be motion *.

In confirmation of this conclusion might be stated some experiments which had previously been made by Mr Pictet, and which prove, in particular, that the caloric excited by friction is not produced by any agency of the surrounding air; since by introducing machinery

* Essays, vol. ii. p. 493.

capable of producing friction into the exhausted receiver of the air-pump, and working it, heat was produced. This indeed had been established by Boyle, by a very satisfactory experiment made in an exhausted receiver, two pieces of brass being made to rub against each other, and a very sensible degree of heat being soon excited *. Mr Pictet, in his experiments, found the heat to be increased by interposing some soft substance, as cotton, between the surfaces subjected to friction: the excitation appeared also to be connected with some electrical phenomena, whence he supposed electricity to be concerned in its production †.

Mr Davy had also, without any knowledge of Count Rumford's experiments, made some of a simi ar nature, from which he drew similar conclusions. By exciting friction, he found heat produced, although the apparatus, as he conceives, was insulated by being placed on ice *in vacuo*; and by exciting it between two pieces of ice itself, he found so much caloric was evolved as to melt it. It seems to be evident, that in this case the evolution of caloric could not be owing to a diminution of capacity, since the water into which the ice was converted has even a greater capactity for caloric. And it is likewise evident, that it could not arise from any chemical action of the atmospheric air, since ice is not acted on by this air, or by any of its principles: In other experiments, too, caloric was evolved when the friction was excited *in vacuo*. Since no cause can be

* Boyle's Works, vol. iii. p. 265.

† *Essais sur la Physique*, p. 197.

pointed out whence the caloric can be derived, supposing it to be matter, Mr Davy, at that time, concluded that it is not material, but is mere motion, or vibration of the particles of bodies *.

In the consideration of this question, respecting the nature of caloric, it is evident, that it is not to be decided, merely from a single difficulty attending one of the hypotheses. A more general view must be taken of the subject. We must inquire which opinion best explains the phenomena of caloric, and which, upon the whole, is supported by the most conclusive arguments.

That the opinion which supposes caloric to be matter, considering it only as an hypothesis, affords a satisfactory explanation of the greater number of the phenomena arising from that power, is sufficiently evident. By the assumption of the existence of a peculiar subtle matter, whose particles are mutually repellent, it is evident, that the expansion of bodies, their fusion, and vaporization, may be easily conceived to arise from its introduction. It is also *à priori* sufficiently probable, that this fluid may have different relations to different bodies, and that from these differences it will produce upon them unequal effects. It may be propagated through them with different degrees of celerity, be contained in them in different quantities, and produce in them different degrees of expansion.

The opposite opinion, that caloric is motion, placing it on the same ground, or considering it as an hypothesis, will be found incapable of explaining these pheno-

* Beddoes' Medical Contributions.

mena in a satisfactory manner. The most general effect arising from the operation of caloric is expansion; but if caloric is nothing but mere motion or vibration of the particles of the heated body, how is this effect produced? Vibration is nothing more than the alternate approximation and retrocession of the particles; but from this state it is evident, that no permanent and uniform increase of volume can take place. Still less can this cause account for the augmentation of volume, which accompanies fluidity and vaporization. When water is converted into vapour, it occupies 1800 times the space which it did while in the fluid form. Suppose vibration to be increased to any intensity, it cannot be shewn how it can permanently separate the particles of a body to such distances.

The deficiencies of this opinion are scarcely less evident in other respects. The laws of its propagation through bodies, for example, are entirely different from the established laws of motion. Were they the same, the propagation of caloric ought to be momentary through elastic bodies, and should be more or less rapid through others, according to their elasticity, which is far from being the case. Neither is any cause pointed out why it should be so slowly transmitted through fluids or airs. We are equally unable to account for its distribution in bodies, and the quantities of it required to produce given temperatures in different substances, or the portions of it absorbed when bodies change their forms, on any laws it could observe, supposing it to be any species of motion.

Not only, however, does the opinion, that caloric is

matter, afford a more satisfactory explanation of the phenomena than the opposite opinion regarding them both as hypothesis,—we have sufficient proofs of a direct kind of the existence of a peculiar calorific matter.

The communication of temperature through a vacuum is such a proof. This fact was ascertained by Pictet, who found, that a thermometer indicated increase and diminution of temperature, when suspended in an exhausted receiver; and Count Rumford himself had shewn what is still more unexceptionable, that this happens when the thermometer is suspended in the Torricellian vacuum. On plunging the apparatus with the thermometer in this situation into a warm fluid, the mercury rose, while it sunk when it was plunged into a cold one, consequently caloric both passed to and from the thermometer, through the vacuum, without any material vehicle by which vibrations could be conveyed. It may be said, indeed, that even in the Torricellian vacuum, a very subtle vapour is present, arising from the vaporization of the mercury from the absence of pressure. There are reasons for believing, that such a vaporization does take place *; but admitting it, the subtilty of this mercurial vapour must be such, that we cannot suppose it capable of transmitting vibrations so as to raise the temperature in a short time; the difference between the conducting power of this vacuum and that of atmospheric air being not more inversely than as 605 to 100, while the difference between the

* Experiments of General Roy, Phil. Trans. 1777.

density of the air, and that of this vapour must be inconceivably great.

The radiation of caloric is another unequivocal proof of its materiality. A matter is thrown from heated bodies, which moves in right lines with great velocity, which is capable of reflection and condensation, which raises the temperature of any body on which it falls, and which in every state preserves the properties of caloric.

Lastly, the existence of caloric in the rays of the sun, apart from visible light, though comprehended perhaps under the preceding fact, adds to the proof, that a peculiar matter exists, possessed of the properties of caloric, and distinct from every other.

The statement of this question, therefore, is now materially altered. While the two opinions which have been the subject of discussion could be regarded only as hypotheses framed to account for phenomena, an important difficulty attached to the one might lead us to question its truth, and from the excitation of caloric by friction, such a conclusion might perhaps have been drawn, as to the material existence of caloric. But when that existence is proved, any such difficulty can be of no weight in invalidating the proof, but must be considered only as arising from our imperfect knowledge of the relations of caloric, and the laws it observes. Were the difficulty, therefore, not removed, it still could not be regarded as disproving the materiality of caloric, though an explanation of this singular phenomenon, could it be given, would, of course, render the theory of caloric more perfect. Several explana-

tions have been proposed. Without discussing what is confessedly hypothetical, I may add the following, uncertain even if it can be regarded as satisfactory.

By friction, percussion, or any other species of mechanical impulse, the particles of bodies must be thrown into vibration or a state of oscillation, they must alternately approach to and recede from each other. In their approach, it is certain that part of the caloric interposed between their particles must be forced out, and in the corresponding retrocession, caloric must be absorbed. Of these propositions there can be no doubt, since it is proved by experiment, that any compressible elastic body, a gas for example, subjected to pressure, gives out part of its caloric; and that on the contrary, in its expansion from the removal of pressure, it abstracts caloric from the surrounding bodies.

The point then to be determined, in order to obtain a solution of the question respecting the production of caloric by friction is, Whence is the caloric derived, which is absorbed by the body in a state of vibration, and which alternates with the quantity given out? If it were merely the quantity given out in the approximation of the particles, that was again taken in in the retrocession, no permanent rise of temperature could take place. But if we could point out any other source whence it could be derived, the whole difficulty would be removed.

Now it is far from being improbable, that the part of the body submitted to friction, and giving out caloric in consequence of it, may receive caloric from the rest of the mass, from the elasticity of that agent, or its tendency to exist every where in a state of equilibrium. In the separation of the particles, ca-

loric may flow in from every side, the layer of matter immediately in contact with the surface in a state of friction, may afford a quantity, which may again be supplied from the matter contiguous to it, and thus a constant evolution may be kept up. Nor is it impossible but that this may extend to a considerable distance from the surface to which the friction is applied, and even through different kinds of matter if they are in contact.

This hypothesis will be much confirmed, if an analagous case can be adduced, in which this very law is observed, and this may be done. When electricity is excited by friction, we conceive the phenomena to be produced nearly in the mode which we have supposed with respect to the generation of caloric. By the vibrations excited by the friction in the electric body, the peculiar fluid which gives rise to the phenomena of electricity is forced out, doubtless by the particles being approximated by the vibration. Now the phenomena of electricity shew, that the fluid thus forced out is not all reabsorbed in the corresponding retrocession of the particles, but that it forms an atmosphere round the electric body, or is carried off by others, while a new portion is received from the matter immediately in contact with the electric substance, and in this manner from the earth itself. Thus a perpetual evolution of electricity is kept up, and the impossible phenomenon of a finite body furnishing an unlimited quantity of a certain power is apparently produced. Caloric may follow the same law, and if this supposition be admitted, the following may be given as the summary of the explanation of the evolution of this power by friction.

The matter which is subjected to friction must necessarily be in contact with some other, and must have a communication with the earth. When the cause producing friction is applied, it is thrown into vibrations; its particles alternately approach to and recede from each other; in the approximation, part of the caloric they contain is forced out; in the retrocession, part of this caloric may be absorbed, but part may be and probably is taken from the surface of matter immediately in contact with the vibrating particles; and thus we have a constant evolution of caloric while the friction is excited.

Count Rumford supposed, that in his experiments the body under friction could not receive caloric from the matter in contact with it, because it was constantly giving out caloric to that matter. But in this there is nothing contradictory; the vibrating body might give out caloric, which would no doubt be diffused in part over the surrounding matter, and it might still receive from it caloric. It might, on the other hand, be supposed, that if the neighbouring matter gave caloric to the body subjected to friction, its temperature must be reduced; but neither does this follow, as the progression may extend gradually through the whole substance, and through the matter in contact with it, and the supply be sufficiently rapid to prevent any reduction of temperature, independent even of the quantity which it again received from the body itself, and by which its temperature is raised.

The evolution of caloric from this cause,—the vibration of the particles of a mass of matter, is no

doubt connected with diminution of capacity; for we have already shewn how intimately related are the capacities of bodies, and the state of their particles with regard to approximation, and by friction, a momentary approximation at least must be produced. And in general terms, it may be said that the increase of temperature from friction, arises from change of capacity produced by a mechanical change in the positions of the particles, the friction causing them to approximate, and lessening the intermediate spaces. But this diminution of capacity, it is to be recollected, is merely momentary, though constantly renewed. The experiment, therefore, of Count Rumford, by which he endeavoured to shew that the evolution of caloric from friction cannot be ascribed to diminution of capacity, is not adverse to this opinion, and indeed in any point of view is of no weight; for the capacity of the matter evolving the caloric was not ascertained while it was in the state of vibration, but after this had ceased, when of course it had returned to its usual state, and when this had even been accelerated and rendered more certain by the metallic filings which were subjected to trial having been gradually heated in the progress of the experiment by which their capacity was ascertained. Suppose the capacity of a body to be diminished from the approximation of its particles by friction, what happens when the friction has ceased? The particles have gradually resumed their former arrangement, and therefore the capacity will have returned to its former state, and the caloric given out will again be absorbed, or its

loss compensated for by absorption from the contiguous bodies. The ascertaining that their capacity in this state is not changed, is not in the slightest degree subversive of the explanation which supposes that when in the state of vibration their capacity is diminished.

It is lastly to be added on this question, that the difficulty may not be so great as at first it appears, nor the quantity of caloric produced by the friction so considerable, compared at least with the condensation which the friction must occasion. Berthollet, who in examining the experiment of Rumford, has referred the production of heat from friction to the disengagemeut of caloric from the approximation of the particles by the pressure applied, and the expansive effort of the caloric through the whole of the mass supplying its place, has justly observed, that a very large quantity of caloric is requisite to produce even a small augmentation of volume in a mass of solid metal, and that of course a small reduction of volume, and therefore an approximation of the particles during friction far from considerable, may evolve a large quantity of heat *.

It has been endeavoured to determine the question with regard to the materiality of caloric, by ascertaining whether it is subject to gravitation, or has weight. It is difficult to make the experiment with accuracy, so as to exclude the operation of circum-

* Chemical Statics, vol. i. p. 412.

stances which influence the result, and hence some of the earlier experiments on this subject, those of Buffon, for example, in which a body appeared to increase in weight by being raised to a white heat, at the rate of 19 grains to the pound, are entitled to no consideration; and those of Roebuck and Whitehurst * seem scarcely to have been made with sufficient care to allow us to place any confidence in their results. Mr Whitehurst pointed out a principal source of fallacy to which these experiments are liable, the ascending current of air from the scale in which the hot body is placed, and the consequent tendency of the portion of air beneath the scale, to restore the equilibrium of pressure, and to this cause he justly ascribed the apparent diminution of weight which in his experiments attended the raising the temperature of a body to a red heat. The contiguity, too, of the hot body to the arm of the balance, must in some degree heat it, and, by the expansion it causes in it, alter the equilibrium.

Dr Fordyce made the experiment in a more unexceptionable manner, by attempting to weigh not sensible, but latent heat; and with this view he endeavoured to ascertain whether the congelation of water, which is attended with an evolution of such heat, be attended with any alteration in the absolute gravity. A glass globe was selected, of nearly three inches diameter, and about 1700 grains of water being put into it, it was hermetically sealed, and when perfectly

* Philosophical Transactions, vol. lxvi.

clean, weighed exactly 2150$\frac{3}{5}\frac{1}{2}$ gr. its temperature being brought to 32°, by having been put into a freezing mixture. It was again immersed in this mixture for 20 minutes, by which part of the water was frozen; it was carefully wiped, and on putting it into the scale, it was found to have gained about the $\frac{1}{60}$th part of a grain. This was repeated five times; at each time more of the water was frozen, and more weight gained. When the whole was frozen, it was found to have gained $\frac{3}{160}$ths of a grain, but the temperature of the globe and contained ice, by having been kept in the freezing mixture, had been reduced to 12° of Fahrenheit. On allowing it to rise to 32°, it was found to weigh $\frac{1}{160}$th gr. more than when the water was fluid. The beam he employed was so adjusted, that with a weight of between 4 and 5 ounces in each scale, $\frac{1}{1600}$th part of a grain made a difference of one division on its index. The air of the room was 37° of Fahrenheit *.

By this experiment, then, it appears that water, by freezing, an operation in which it evolves caloric, becomes heavier, and that of course the addition of caloric to a body renders it absolutely lighter; which, if admitted, appears to prove that caloric counteracts the attraction of gravitation, as it does that of contiguous attraction or affinity.

The experiment was repeated by Morveau and Chaussier, and with the same result, the water being heavier after it had been frozen in glass vessels her-

* Philosophical Transactions, vol. lxxv. p. 361.

metically sealed, than it was before. Two pounds of sulphuric acid weighed three grains less when it had recovered its fluidity, than it weighed when it was in a congealed state. Fontana, however, in repeating these experiments, did not find that there was any sensible difference in the weight of the ice and water, the balance remaining in perfect equilibrium *.

Lavoisier introduced into a very strong glass flask a small capsule, on which were placed six grains of phosphorus. Having closed it accurately and firmly, he weighed it with great exactness, and removing it, kindled the phosphorus, by exposing it to the solar rays, concentrated by a small lens. When the vessel had become cold, it was again weighed, and not the smallest difference of weight could be discovered. In a second experiment, much more conclusive, he put a pound of water into a thin glass flask, which he sealed hermetically, and then weighed with the most scrupulous exactness, in a balance, which, when loaded with from 18 to 20 ounces, vibrated with the tenth of a grain. The water was frozen, and the vessel, on being dried and again weighed, was found to be exactly the same; nor was any difference discoverable whether it was weighed with the included matter in the state of water, or in the state of ice †.

Lastly, the experiment has been made with every precaution, and in a manner that appears unexceptionable, by Count Rumford. He chose two Florence

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* *Journal de Physique*, t. xxvii. p. 268.

† *Mémoires de l'Acad. des Sciences*, 1783, p. 418.

flasks perfectly alike, and putting into one a quantity of distilled water, amounting to 4107.86 grains, he also put into the other the same weight of weak spirit of wine, sealing both the bottles hermetically, and wiping them perfectly clean and dry. They were suspended from the arms of a very sensible balance, and brought into exact equilibrium. They were then exposed to an atmosphere of the temperature of 29° of Fahrenheit for 48 hours. On being examined at the end of that time, the water in the flask was converted into ice, and the arm of the balance to which it was attached preponderated. The increase of weight which the water appeared to have gained by its freezing, was found by what was necessary to restore the equilibrium, to amount to $\frac{1}{33904}$ of its whole weight at the beginning of the experiment.

The result appeared, therefore, to correspond with the experiment of Fordyce. Count Rumford, however, by varying the experiment, found reason to conclude that he had been deceived. In two bottles, as nearly alike as possible, he put equal weights of water and quicksilver, and suspending them to the arms of the balance, he allowed them to acquire the temperature of the air of the room, 61°, and brought them into perfect equilibrium; they were then exposed for 24 hours to an atmosphere at 34°, but without either of them acquiring or losing weight. Yet, from the respective capacities of water and quicksilver, it is certain, that in that reduction of temperature, the former must have given out much more caloric than the other; the difference, however, produced no dif-

ference in weight. Had a difference existed, amounting even to the one millionth part of the weight of either of the fluids, such was the delicacy of the balance, that it would have been discovered. He also repeated the first experiment with every possible precaution, exposing the equal bottles, with water and spirit, small thermometers being included, to an atmosphere of 30° for 48 hours. At the end of that time the included thermometers, as well as one suspended in the air of the room, indicated the temperature to be 29°, and the two bottles were in the most perfect equilibrium. He adds, that he afterwards repeated the experiment several times, and in no instance did the water on congealing appear either to gain or lose weight. But if the bottles were weighed when they were not precisely of the same temperature, they would frequently appear to have gained or lost, either, as he supposed, from the vertical currents which they caused in the atmosphere on being heated or cooled in it, or from unequal quantities of moisture condensed from the atmosphere on their surface, or from these causes conjoined *.

From the whole of the experiments that have been made with accuracy on this subject, it may be concluded, that if caloric be possessed of weight, it exists at least in such a state of rarity that its gravity cannot be ascertained by experiment. It is obvious, however, that this does not afford even a presumption against its existence as a material principle; and when

* Philosophical Transactions, 1799, p. 179.

its extreme subtilty, demonstrated by the facility with which it penetrates all bodies, is considered, we can scarcely expect, *à priori*, that, by any of our instruments, it should be discovered to have weight.

Sect. VII. *Of the sources of Variations of Temperature, and the application of these to Practical Chemistry.*

The consideration of the subjects announced in the title of this section will conclude the Chemical History of Caloric.

As the tendency of this power is to diffuse itself over bodies until an equilibrium of temperature is established, such an equilibrium would be attained, were there no foreign causes to counteract this tendency, and the temperature of the globe would at length settle at that point which would be the medium between the temperature of the different substances of which it is composed, or rather the temperature would have been always uniform, and proportioned to the quantity of caloric assigned to the earth.

Such an uniform temperature would, however, be altogether incompatible with the economy of nature; it is therefore obviated by the constant operation of various causes; and no where do we trace more perfect arrangement than in that by which a certain range of temperature is established, in which the succession of changes is adapted to those operations that require

it; while extremes, either of heat or cold, are constantly counteracted, and are at least prevented from spreading over the globe.

The great source of natural heat is the solar rays. These pass through the atmosphere without producing much augmentation of temperature; but when arrested by opaque bodies, the radiant caloric which is intermixed with the visible light is retained, and heat produced. As every part of the earth's surface is not equally and at all times to the same extent exposed to the action of the solar rays, inequality of temperature giving rise to variety of climate, and change of season is established. The extreme of temperature, however, which might prevail, and accumulate in those parts of the globe most exposed to this source of heat, is counteracted by other causes constantly operating, and capable of preserving it within certain limits. The principal of these are the rarefaction of the atmosphere and the evaporation of water. When the earth is much heated, the air immediately incumbent on it receiving caloric is expanded, becomes specifically lighter, and ascending through the atmosphere, its place is supplied by new portions of air from each side, which in their turn are heated, expanded, and rise. An ascending current is thus established, by which the accumulation of heat is prevented where it is already abundant, while the warmer air must, by the constant succession, be propelled to colder climates, and in its course will gradually part with the caloric it had received.

At the same time, when heat accumulates, the eva-

poration of water becomes more copious; in passing into vapour it absorbs much caloric without increasing in temperature, this vapour ascends in the atmosphere; when the heat diminishes, or when wafted to colder regions, it is condensed, and gives out the caloric it had formerly absorbed. In seasons or situations where the cold becomes still more intense, it is congealed; and in suffering this change it still evolves caloric, to moderate the progressive reduction of temperature. When warmth is restored, it returns to the fluid state, again absorbs caloric, and thus softens the transition of seasons. Sudden and extreme variations are more effectually guarded against, and the temperature of the globe every where preserved more uniform. These important operations are all dependent on change of capacity from chemical action, or change of form.

The range of natural temperature is comparatively moderate. The medium heat of the globe, and which at a certain depth, that of 1000 feet from the surface, is in every country found to be the same, is about 50° of Fahrenheit. The average annual heat in the torrid zone is from 75° to 80°, in moderate climates 50° or 52°, and towards the polar regions 36°. The extremes over the whole globe extend from a few degrees above 100° of Fahrenheit to 50° below the zero or commencement of the same scale. In tropical climates the heat in the shade occasionally rises to 105° or even 110°. The latter temperature has been observed at Pekin in China. At Senegal the air in the shade is mostly heated to 94°, and near that place is frequently at 111° by day. At Pondicherry, it is said

to have been at 113° or 115° *. With regard to cold, in northern climates—Siberia and Hudson's Bay, the temperature is every year so low as to freeze quicksilver. At Hudson's Bay, the spirit thermometer was observed in the open air to stand at —50° †, and there is no reason to believe that any natural cold yet observed much exceeds this. At one time, indeed, it was supposed, that much more intense colds prevailed, the mercurial thermometer having been observed to sink 300 or 400 degrees below the freezing point of water; in one case observed by Mr Hutchins, even to 490 ‡. But it has been already shewn, that in this there is a deception, from the very great contraction which quicksilver experiences in becoming solid, and which of course causes these descents in the thermometrical tube. And when, at the same time, and exposed to the same atmosphere, observations were made with a spirit thermometer, the descent was not greater than what corresponded to — 46°. The cold of America even exceeds that which prevails under the same latitudes in Europe; we have, therefore, no reason to believe, that in the old world more intense natural colds occur than in the new, and from the descriptions given of their effects, they appear as severe in North America as in the north of Europe or Asia.

The range of temperature, as produced by artificial

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* Kirwan on the Temperature of different latitudes, p. 93. 99. 101.

† Philosophical Transactions, vol. lxxvi. p. 271.

‡ Ibid. vol. lxxiii. p. 386.

arrangement, is much greater. Our power of producing cold is not yet indeed great, compared with that of exciting heat. The cold we obtain by freezing mixtures does not much exceed 100 degrees below the freezing point of water. Fourcroy and Vauquelin, by a mixture of snow and muriate of lime, previously cooled, effected a reduction of temperature to 97° of Fahrenheit below that point, when the temperature of the atmosphere was not much below freezing. Mr Macnab, from a mixture of snow with diluted sulphuric acid obtained a cold equal to — 78°½ of Fahrenheit, or 110°½ below the freezing point of water *. And Mr Walker, by successive cooling of the materials, obtained from diluted sulphuric acid and snow, a reduction to — 91°, or 123° below the freezing point of water, the greatest degree of cold yet known †.

The highest heat that has yet been measured is equal to about 160° of Wedgwood's, or 21,877° of Fahrenheit's scale. This was the temperature of a small air-furnace belonging to Mr Wedgwood, and is superior to that which is necessary to fuse cast iron, or to bake porcelain. From the effects produced in the focus of a powerful lens or speculum by the concentration of the solar rays, there can be no doubt that the heat there is still more intense, as is also that excited by a stream of oxygen gas directed

* Philosophical Transactions, vol. lxxvi. p. 266.

† Ibid. for 1801.

on burning charcoal; but of these we have no exact measurement.

Were the chemist restricted to those variations of temperature which occur in nature, he would be little more than an observer of her operations, since these are too trivial to have much influence on the operations of art. It is in our power, however, to produce more intense degrees, both of heat and cold; and in the remaining part of this section I have to state the means by which these are accomplished, and the various contrivances by which these are applied and regulated. This will include a description of several of the most important operations and instruments of Practical Chemistry.

THE sources of heat which are under the control of art, and which, by peculiar arrangements, may be increased and applied, are the Solar rays, Electricity and Galvanism, Condensation, Mechanical action between solids, including Friction and Percussion, and Chemical action, to which head Combustion belongs.

The Solar Rays are powerful in producing heat. In the open air, a thermometer is raised, by free exposure to them, to above 100°; and when inclosed, so as to prevent the effect of a current of air, it may be raised much higher. In some experiments of this kind by Saussure, the thermometer, by the action of the solar light, was raised to 201°; the temperature of the external atmosphere being 75°. And Professor Robison, in repeating these with a similar ar-

rangement, obtained a rise of 230°, and even 237° of Fahrenheit's scale *.

When the solar rays are concentrated by a lens, or by a concave mirror, heat is excited to a degree of intensity nearly equal to what can be produced by any other arrangement. By very large burning-glasses, such a heat is excited in the focus, as is sufficient to melt the greater number of the metals and the earths, and to dissipate many other substances in vapour. It appears from the experiments of Macquer, that a greater heat may be excited by a concave mirror than by a lens; but the former is inconvenient, and indeed scarcely practicable in its application, from the rays being reflected upwards, and it being necessary, therefore, to suspend the body designed to be acted on in the air. The use of either, indeed, is very limited, for the heat, though powerful, is excited only on a small point; hence it can be applied to scarcely any other purpose, than to discover the changes which bodies suffer from intense heat. A number of experiments of this kind have accordingly been made, and are recorded in the Memoirs of the Academy of Sciences. Count Rumford has shewn, that the intense heat obtained in the focus of a lens, arises entirely from the concentration or condensation of the rays of light, in other words, from the number of them brought to act on one point, and not, as some natural philosophers had supposed, from their power

* Black's Lectures, vol. i. p. 546.

being augmented by a change in the direction of their motion; the same quantity of solar light, directed on the blackened surface of a metallic vessel containing water, producing in it the same total rise of temperature, whether the rays were parallel, or were made to converge by a lens.

The Electric Discharge is capable of producing a very sudden and great heat. If from a powerful battery, and transmitted through metallic wires of small diameter, they are instantly fused, even though of those metals which suffer this change with the greatest difficulty. From this property, the electric discharge, as I shall afterwards have to remark, is applied to effect the combinations of those gases, which do not unite at a low temperature.

The Galvanic Discharge is likewise very powerful in exciting heat. On establishing a communication between the two extremities of the arrangement producing galvanism, a high temperature is excited at the point where the communication is momentarily completed and interrupted; and in this way every combustible body may be made to burn, and many incombustible substances are fused. Or if a very fine metallic wire, as iron-wire, form part of the circuit of a powerful galvanic arrangement, it will be melted by the heat which the galvanic energy excites in its passage. This source of heat has scarcely been applied to any important chemical purpose.

The production of heat from Condensation, is most clearly exemplified, in substances which are highly compressible and elastic, consequently in

aëriform fluids. It has been long known, that by condensing a gas by mechanical pressure, its temperature is raised; that in allowing it to expand again, its temperature falls; and that by rarefying it still farther, a degree of cold is produced. I have already alluded to these facts, as illustrative of the cause of the capacities of bodies for caloric. I have now to state them rather more in detail.

The changes of temperature, from rarefaction and condensation of aëriform fluids, as they are indicated by a thermometer suspended in the air, do not appear very considerable, amounting only to a few degrees of Fahrenheit. The rise and fall of the thermometer, however, are very sudden, and this led Mr Dalton to suspect, that the real change in the temperature of the air is much greater than it appears to be from the indication by the thermometer; but that the inequality exists only for a few seconds of time, owing to the containing vessel having a surface so much more extensive than the thermometer, that it speedily checks the change of temperature, by abstracting, or by yielding caloric. The quantity of matter, too, in the bulb of the thermometer, being so much greater than that in the rarefied air, notwithstanding the difference of their capacities, more effect is produced in the temperature of the latter, by the evolution or absorption of caloric, than in the temperature of the former by the communication or abstraction of the caloric thus evolved or absorbed. Thus the phenomena agree with the supposition of great heat or cold being pro-

duced by the condensation or rarefaction, but existing only for a very short time *. What also proves it, is the observation of Lambert, that, in rarefying air, the cold is greater the more quickly the rarefaction is performed.

This view accords well, too, with a fact since established, that, by a very sudden and great condensation, a very high temperature, equal even to ignition, may be produced. It had been known for some time, that a luminous appearance is sometimes produced by the discharge of an air-gun in the dark †. The experiment was repeated before the French National Institute. From the air rapidly compressed in the ball of an air-gun, so much heat was disengaged from the first stroke of the piston, as to set fire to a piece of fungus match placed within the pump. And if the body of the pump be terminated by a moveable end, formed of a piece of steel, with a glass lens in its centre, at the stroke of the piston, a ray of vivid light is seen in the inside, which is suddenly disengaged ‡. Biot afterwards succeeded in causing the union of oxygen and hydrogen gases, and the consequent formation of water, by compressing rapidly a mixture of them in the syringe of the air-gun. The experiment is a very hazardous one, as, in two out of three times that it was repeated, the barrel was burst by the ex-

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* Manchester Memoirs, vol. v. p. 515.

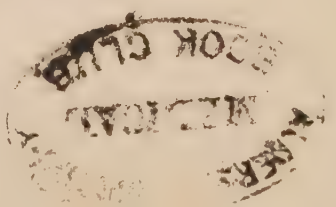
† Nicholson's Journal, vol. iv. p. 280.

‡ Ibid. vol. ix. p. 302.

plosion *. From the experiment itself, it might be doubted, whether the compression first caused the combination of the gases, by the approximation of their particles, and that then the heat was evolved as the consequence of this, or whether it merely produced such a heat as caused the combination. The preceding experiment, however, renders it probable, that the latter is the real *rationale*, though it would be interesting to repeat it on an individual aëriform body, to render it more decisive.

That species of mechanical action which excites strong vibration in the particles of solid bodies, as Friction and Percussion, is productive of increased temperature. Of heat from friction we have many familiar examples. Two pieces of hard wood, rubbed against each other, are so much heated as to be kindled; and among savage nations, this method is often had recourse to, to procure fire. The friction on the axle of a loaded carriage, is sometimes such as to cause it to take fire, as is that from a rope made to revolve rapidly round a solid body. The intensity of the heat from friction, depends not only on the force of the friction, but also on the state of the bodies subjected to it, with regard to hardness, elasticity, and other qualities. Scarcely any accurate experiments have been made on this subject. It is known, however, that the hardest substances do not afford the greatest heat. A table is given in Nicholson's Journal, (vol.

* Nicholson's Journal, vol. xi. p. 303.



viii. p. 218.), of a series of experiments on the heat produced by rubbing different kinds of wood against each other; whence it appears, that the heat produced is not either directly or inversely as the hardness. One singular fact is added, that the heat is greater when the pieces subjected to friction are rubbed in the direction of the grain of the wood, than when the grains of the woods cross each other.

The heat from percussion is no doubt produced in the same manner as that from friction. It is easily carried to the same extent. By hammering an iron-rod on the anvil, it is raised to a red heat; and the sparks struck from steel by a flint, consist of particles of steel raised to a high temperature by the percussion, and rising to a state of ignition by suffering a real combustion in passing through the atmosphere. Hence, in making the experiment *in vacuo*, the particles struck off are not luminous, though their temperature is probably not far distant from a red heat. Such a temperature can be produced from mechanical action alone, as we find it to happen in incombustible matter. Putting aside the examples from phosporescent bodies, which are undoubtedly fallacious, this is proved by a very decisive experiment made by Mr T. Wedgwood, that of bringing a piece of window-glass in contact with a revolving wheel of grit, when it became red-hot at its point of friction, and gave off luminous particles, which were capable of inflaming gunpowder *.

* Philosophical Transactions for 1792, p. 45.

The heat from friction or percussion is not employed in practical chemistry.

I have already stated the difficulty with regard to the explanation of the augmentation of temperature from these causes, and the light in which it is to be regarded, as connected with the theory of caloric. The heat produced, it can scarcely be doubted, is chiefly to be ascribed to a momentary diminution of capacity, from the approximation of the particles of the body under friction or percussion. It is not unlikely, that the excitation of electricity, which will accompany the friction, may likewise have some share in its production.

Chemical action is an abundant source of variation of temperature; the temperature being sometimes elevated, sometimes reduced. The theory of both changes has already been explained: More immediately they may be referred, according to the view which Berthollet has taken of the subject, and which has been stated under the Chapter on Affinity, to the condensation which accompanies chemical action, modified by the change of form which so frequently takes place also at the same time: Or, ultimately, they depend, according to the theory of Irvine, on the change of capacity which follows combination, heat being produced when the capacity of the product of the combination is inferior to the mean of the capacities of the substances combined, and cold in the opposite case where it is superior to that mean.

Of the varieties of chemical action productive of heat, and indeed of all the sources of increased tempe-

rature, combustion is the most important, both for common purposes, and in the operations of chemistry. To explain in a general manner the principles on which combustion is most effectually excited and applied, it is necessary to observe, that it is dependent on one of the constituent principles of the atmosphere, —oxygen gas. At temperatures which in the greater number of cases require to be considerably elevated, this principle combines with those bodies which we name combustible or inflammable ; the combination is attended with the production of heat, and in general with the evolution of light, and it is this process which constitutes combustion or burning.

We can therefore at once perceive how much combustion must be dependent on a due supply of atmospheric air to the combustible body ; and accordingly it is more rapid the more freely the air is applied. On this is founded the construction of Furnaces, which, under various forms, are employed in many of the processes of chemistry as well as in the chemical arts, to excite and apply heat.

The essential parts common to every furnace, are the body or fire-place, in which the fuel and the vessel containing the materials to be operated on are placed ; the chimney, by which the smoke and heated air escape, and the ash-pit, into which the ashes fall, and by apertures in which air is admitted to the burning fuel.

The principles on which the production of heat in furnaces depends, are, that inflammable matter cannot burn without the access of air, and that the rapidity

of the combustion, and consequently the quantity of heat produced in a given time, are proportioned to the quantity of air transmitted over the burning matter. When fuel is placed in a closed cavity, like that of a furnace, connected with a chimney, and kindled, the air in the upper part of the furnace is rarefied, and ascends by the chimney; the pressure of the external atmosphere forces a quantity of fresh air through the openings below, which, rising through the mass of fuel, occasions a strong combustion.

In furnaces, therefore, the strength of the combustion depends on two circumstances,—the access of atmospheric air from below, and the due height and width of the tube containing the column of heated air. The first is regulated by registers, consisting either of a number of apertures, fitted with brass stoppers, or what is more convenient, a moveable semicircular plate, adapted to one aperture of sufficient size. The second principally contributes to the rapidity of the combustion. When the tube or chimney is lengthened, the difference between the specific gravity of the column of heated air which it contains, and that of the column of external air being greater, a larger quantity of fresh air is constantly forced through the fuel, and a strong draught, as it is termed, is formed. This is proportional to the height of the chimney, at least to a certain extent; for, beyond a certain height, the temperature of the air being reduced, the difference in specific gravity becomes less, and no advantage is gained. The same advantage is obtained, by causing the air which passes into the furnace to pass through

through a long tube, disposed horizontally, and connected with the ash-pit, which in this case is rendered as much air-tight as possible; as thus a still greater difference is established between the external and internal columns of air in weight. The narrowing the tube has to a certain extent a similar effect, though, if it be rendered too narrow to admit of the free exit of the air, and of any smoke of the fuel, the rapid circulation will be impeded. Notwithstanding the importance of these circumstances in the construction of furnaces, the due proportions of height and width of the chimney to the diameter of the cavity of the furnace, have not been very well ascertained. Macquer, from some trials, states that the diameter of the tube ought to be to that of the furnace as 2 to 3 nearly; and that when the internal diameter of the furnace is 12 or 15 inches, if the diameter of the tube be 8 or 9, and its height 18 or 20 feet, a very intense heat is excited.

In the construction of furnaces, another important object is the confining the heat or preventing its dissipation. This is accomplished by coating the internal surface with some substance which transmits the heat slowly, as a lute of clay and sand, which likewise serves to defend the substance of which the furnace is made, from the action of the fire. This is necessary at least when the furnace is a moveable one, constructed of metallic plates. When fixed, and built of brick, the building is a sufficiently imperfect conductor to confine the heat.

A very convenient general furnace, applicable to

most of the operations of chemistry, was contrived by Dr Black. It is represented Plate VII. Fig. 52. A is the body of the furnace, of an elliptical form, which contains the fuel, and frequently the substance which is to be operated on, made of plate-iron, and lined to the thickness of 2 or 3 inches, first with a mixture of clay and charcoal, beat into a paste with water, and over this, next to the fuel, with a coating of clay and sand, the coating being thicker towards the bottom, so as to diminish the cavity, and render it slanting downwards from the chimney. On the top of the body is fixed an iron plate, having two apertures, one, *a*, placed over the cavity, and designed to receive an iron pot with sand, when evaporation, distillation, or any similar process is performed; the other smaller, to which the chimney, B, made of a tube of iron, is fixed. C represents the grate, in a plate of iron which is fixed to the bottom of the body of the furnace, nearly, but not exactly opposite to the larger aperture in the upper plate. D is the ash-pit, the body of the furnace being closely received into it, and resting on a strong ring which runs round the cavity, at about half an inch deep. In thisash-pit is a door, *b*, turning on hinges, to remove the ashes; and a register, *c*, designed to regulate the admission of air. It is a plate of iron, in which are six apertures, filled with plugs; the size of them increases in geometrical ratio, so that by opening them singly, or in combination, the supply of air to pass through the fuel, and consequently the heat to be excited in the furnace can be regulated with precision. The fuel is introduced at the top, but as

it cannot easily be supplied this way in the progress of the process going on in the furnace, at least when the sand-pot is used, the furnace is sometimes constructed with a door in the side, though this renders the regulation of admission of air less perfect. When the furnace is used for fusion, or similar purposes where a sand-pot is not required, the upper aperture is covered with a dome.

Furnaces applied to particular purposes, as the assay-furnace, used in assaying and other operations on the metals, or the reverberatory furnace, in which by a dome the flame is made to reverberate on the substance operated on, are little used by chemists. It is an object of considerable importance, however, to have a furnace capable of exciting a very intense heat, and different kinds of what, from the use to which it is applied, is named a melting-furnace, or, from the strong blast of air which is forced through it, a wind-furnace, have been proposed.

One of the most simple, and which perhaps is equal in power to any, is that invented by Pott, and employed by him in his numerous experiments on the fusibility of earthy mixtures, Fig. 54. The body of it, A, is of strong sheet-iron, coated with crude clay, which has been wrought into a paste with an equal portion of baked clay, and a sufficient quantity of blood. The dome, B, is likewise constructed of sheet-iron, and coated in the same manner. A small aperture, *a*, is in the front of it, through which fuel is introduced, and a long tube, C, is connected with it as the chimney. It is obvious, that the longer this tube

is, the current of air passing through the fuel will be more rapid, and therefore the combustion will be more vivid. It can easily be lengthened by connecting another tube, D, of the same diameter with it, and a similar advantage is gained by bringing a tube, disposed horizontally, into the ash-pit *b*, through which the air is admitted, adapting it accurately to the aperture. Coaked coal is the proper fuel, and it requires to be frequently supplied.

Another convenient portable melting furnace, is that described by Schmeisser, Fig. 53. This too is formed of iron-plates, coated with clay and sand; the cavity being about 12 inches in height, and 6 inches wide, having a dome which terminates in a tubular chimney, about 2 inches in diameter. Besides being adapted to excite a very intense heat, it may be applied to various purposes, and is, therefore, so far a general furnace. For cupellation, a muffle can be introduced at the door, *a*; for distillation in the naked fire, an earthen retort may be placed in it, the neck resting on the aperture *b* in the dome; *c c* are apertures in the sides opposite to each other, through which an iron or earthen tube may be passed, so as to be kept at a red heat; *d* is an aperture to which the nozzle of a double bellows may be adapted to excite a violent heat when it is required; *e* is the ash-pit door; *f* a moveable register, by which the admission of air may be regulated.

In operations on a larger scale, a fixed furnace built of brick is required. Fig 55. represents a convenient form of a melting furnace of this kind, the structure of which is obvious from the figure. A is the cavity of

the furnace, terminating by a curved passage in the chimney B, which is raised to the requisite height. At C is an aperture covered with a thick plate of iron, or of fire-brick, through which fuel is introduced. On the grate, D, is placed a small covered crucible, on a pedestal of baked clay, and in the passage of the chimney, at *a*, a muffle is sometimes placed; E is the ash-pit, through which the air is admitted to the fuel.

Small furnaces which may be placed on a table, and which are useful for experiments on a limited scale, have also been constructed of the large black lead crucibles or pots. A furnace of this kind was described by Lewis, which has been so much improved by Mr Aikin, as to be capable of producing a very intense heat *.

When solid substances are to be exposed to these intense heats to fuse them, or to favour their mutual chemical action, crucibles are the vessels generally employed, at least for experimental purposes. These are of different materials, according to the purpose for which they are to be used. The Hessian crucible, as it is named, is of a species of earthen-ware or baked clay, which stands the most intense heat without fusing, and which is most generally used; the only disadvantage attending it is, that it is liable to be cracked by very sudden alterations of temperature. The black-lead crucibles, made of plumbago and clay baked, are not liable to this, and are, therefore, often used, especially in fusing metals; from a number of saline substances, however, they suffer corrosion. Both are made narrow at the bottom, that the fused matter may

* Philosoph. Mag. vol. xvii. p. 146.

be collected into a small mass, and either triangular, or if round, pinched at the mouth, that the melted matter may be poured out. The usual forms are represented, Fig. 56, 57. When placed in the furnace, a small clay pedestal is placed on the grate, on which the crucible stands, to remove it from the application of the current of cold air; and a cover is adapted to the mouth, to exclude the fuel. Crucibles of platina are likewise sometimes used. Cupels, which are used in some similar processes, are small cups made of bone-ashes, very porous: they are used principally in refining the more precious metals, which are not oxidated by heat and air, any oxidable metal combined with them, soon suffering this change, and the vitrified oxide being absorbed by the cupel. They are placed under an arched earthen vessel, open at the end, named a Muffle, Fig. 58. by which, while the fuel is excluded, the air which is necessary in the process is freely admitted.

In applying a more moderate and equable heat to favour chemical action, the medium of sand, forming the Sand Bath, is generally employed, and glass vessels named Matrasses or Cucurbits are used. The cucurbit is represented, with the alembic, Pl. VI. Fig. 42. as the apparatus which is used in sublimation. The matrass is represented Fig. 45: from being blown thin and equable, it sustains alternations of temperature with less risk of breaking, and from its long neck any vapour which is formed is condensed and falls back.

A very convenient method of applying a heat from combustion, where it is not necessary that it should be very intense, is by the Lamp-furnace. A lamp with

a concentric wick, and internal supply of air, on the principle of Argand's, affords a heat which has the advantage of being very easily regulated; the elevation or depression of the wick, and the distance at which it may be placed from the body designed to be heated, allowing the application of various degrees of heat, and their speedy change. By an invention of Mr Webster, in which a double concentric wick is placed in the lamp, the heat is rendered more powerful, at least three times more so than when the lamp with a single wick is used *.

The lamp is sometimes attached to an iron or brass rod, on which it slides, and to which are also attached rings of different diameters, to support a retort or matrass above the flame. It is more convenient to have a detached standard with such rings, which can be inserted in a socket, that slides on the rod of the standard, and by a thumb-screw can be fixed at any height.

A mode of applying a very strong heat at a small point, is that by the Blow-pipe. This instrument is merely a conical tube, with a very small aperture at its narrow extremity, and having towards that extremity a moderate curvature. It is made of brass, or better, and more commonly of glass; it being much easier to give a glass tube a fine and smooth aperture. By blowing through this tube on the flame of a candle or lamp, in a horizontal direction, the flame is urged in a conical form, and at the extremity of it, or rather at the extremity of an internal blue flame, which is surrounded by one of white light, a heat compara-

* Philosoph. Mag. vol. xiv.

lively intense is excited. To condense the humidity of the expired air, there is an enlargement or swell at one part of the tube; and when constructed of brass, small moveable nozzles are adapted to the tube, having holes of different diameters, to afford a larger or smaller flame. This instrument is used by the chemist and mineralogist, in ascertaining the fusibilities of bodies. A fragment of the substance to be submitted to trial, not exceeding the size of a pepper-corn, is placed on a piece of solid charcoal, or in a spoon of silver or platina, and the flame is directed upon it, or if its fusion is to be promoted by the addition of any flux, it is reduced to powder and mixed with it. It is also much employed by the artists, in enamelling and in working on glass, which is melted by it, so as to be capable of being moulded into any shape, or blown into vessels of a small size.

The facility of blowing through the blow-pipe, so as to keep up a constant stream of air, is not very easily acquired, and it is always fatiguing to continue it for any length of time. Different contrivances have been had recourse to, to obviate this inconvenience. The instrument is sometimes connected by a flexible tube with double bellows worked by the foot, by which, if the bellows be well constructed, a strong and uniform stream of air is forced through the tube *. It is difficult, however, to construct bellows which shall be nearly air-tight: hence a great part of the air

* Cronstedt's Mineralogy by Magellan, Appendix.

escapes without passing through the blow-pipe. To obviate this, Mr Hare has constructed a hydrostatic blow-pipe, of which he has given a description *. Abbé Melograni employs two glass globes, connected by their necks. One of them being half filled with water, is placed so that the water shall run into the other, forcing a stream of air through a tube which issues from it, and which is directed on the flame of a candle †. Lastly, the vapour of spirit of wine has been applied to this purpose; a quantity of spirit being put into a small vessel, which is placed over the flame of a lamp, is soon converted into vapour; this vapour conducted through a curved tube is directed on the flame of a candle, or that of a wick placed in a different part of the same tin lamp as that by which the spirit is heated. A safety valve is likewise adapted to the vessel containing the spirit ‡. Even with this, however, the flame is not so equable as that urged by a current of air, propelled in the other modes.

Since, by the contrivances hitherto described, combustion is rendered more rapid, and of course a stronger heat is produced from the air being more rapidly supplied to the combustible matter, it may easily be perceived, that if we employ not merely atmospheric air, but the constituent part of it, oxygen gas, which more peculiarly supports combustion, a still

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* Philosophical Magazine, vol. xiv. p. 238.

† Nicholson's Journal, vol. ix. p. 25. and 143.

‡ Ibid. vol. iii. p. 1.; vol. iv, p. 106.

more intense heat will be excited. In this way, accordingly, we can raise the highest heat which can be obtained by artificial arrangements.

The method that has been employed is to form a small cavity in a piece of charcoal, which is then kindled by directing flame, urged by a blow-pipe upon it; the substance designed to be operated on is put into the cavity, and a stream of oxygen gas is directed from a tube with a small aperture which communicates with a gazometer containing the gas, on the red hot charcoal. The combustion instantly becomes vivid, and a very intense heat is excited. A series of experiments were made in this manner by Lavoisier. All the metals were melted, and with the exception of platina were even either dissipated in vapour or made to burn. The simple earths, with the exception of lime, magnesia, and barytes, were fused. And all the compound earthy fossils were either melted into a species of glass, or softened, and in general their colours were destroyed. The heat, it is remarked by Lavoisier, is superior to that excited by the concentration of the solar rays by the most powerful burning glass, as in the focus of the great burning glass of Tschirnhausen, platina is either not changed, or after long exposure is only agglutinated; and argil, jasper, and several other fossils, suffer no alteration, while on the burning charcoal, excited by oxygen gas, all these substances are quickly fused *. If the stream of gas be urged on the

* *Mémoires de l'Acad. des Seiences*, 1783, p. 563.

flame of a lamp, a very intense heat is also excited, though inferior to that from burning charcoal.

Ehrman prosecuted these experiments, and in his work * are detailed the results, almost every mineral substance having been subjected to trial. He appears to have been able to excite a more intense heat than that obtained by Lavoisier, as he volatilized platina, and fused barytes and magnesia, lime being the only earth, and indeed the only substance, which was perfectly infusible †. A series of similar experiments, principally on the gems, performed by a philosophical society in London, is related in the eighth volume of the Philosophical Magazine.

Another method has more lately been employed of increasing heat by oxygen gas, that of presenting a current of it to a current of hydrogen gas, and kindling the stream of the mixed gas. A most intense heat apparently superior even to that in the former mode, is thus obtained. This application has been suggested by Mr Hare. Each gas may be allowed to issue from a separate gazometer, and being united in a common metallic tube, of small width and length, the mixed stream may be kindled at the aperture of the tube. The heat existing in the centre, or towards the point of the flame, is even more intense than that produced by directing oxygen gas on burning charcoal. This is proved by barytes being completely fused by it, which was found infusible by Lavoisier in the other method. An account of expe-

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* *Essai d'un Art de Fusion.* † *Ibid.*

riments performed by it, and of the apparatus with which they were performed, is given by Mr Hare *.

Having described the means of producing augmentation of temperature, and their application to practical chemistry, I have, lastly, to state the methods which may be employed to reduce temperature, or produce cold. These are Rarefaction, Evaporation, and Chemical action.

I have already stated, that when, by the removal of pressure, a gas is suddenly rarified, or allowed to expand, its temperature is reduced. This is apparent, even in the comparatively slow rarefaction of air in working the air-pump, a thermometer in the receiver sinking, as Dr Cullen long ago remarked, two or three degrees. Dr Darwin observed, that if, in the stream of air issuing from the receiver of an air-gun, in which it had been compressed, a thermometer were placed, it sunk 5 or 7 degrees. The striking phenomena observed in the fountain of Hiero, constructed on a large scale at the mines of Chemnitz, in Hungary, is, however, the best example of the production of cold, by rarefaction. In this engine, the air in a large vessel is compressed by a column of water, 260 feet in height; on opening a stop-cock, it rushes out with great violence, and in expanding, the watery vapour which existed in it, is not only deposited, but is congealed, falling like snow, or adhering in icicles to the aperture of the stop-cock †.

* Philosophical Magazine, vol. xiv. p. 301,

† Philosophical Transactions, vol. lxxviii. p. 43.

Cold from this source, it is obvious, cannot be applied to any practical purpose.

The production of cold from evaporable fluids exposed to the atmosphere, had been noticed by Mairan and by Wilcke, but was first made the subject of accurate experiment, and ascribed to the evaporation of the fluid, by Dr Cullen. A thermometer, when its bulb was immersed in spirit of wine, sunk always several degrees on suspending it in the air, but recovered its temperature when it had become dry. With other fluids the same phenomenon was observed, though not precisely to the same extent. With water it was much less, and with ether considerably greater *.

From these experiments, Dr Cullen remarked, that the cold produced is greater as the fluid is more evaporable. He found, too, that it is increased by whatever accelerates the evaporation, as by a current of air being directed on the wet bulb. If it be wet with water, and the evaporation promoted by blowing a current of air on it, the temperature sinks about 5 degrees of Fahrenheit; if with alkohol, it falls 12 degrees; and from sulphuric ether the fall is above 30 degrees. If the ether be evaporated, therefore, from a small tube containing water, the water will be frozen by the cold produced. If a piece of linen be wrapt round the bulb of a thermometer, be well moistened with rectified ether, and exposed to a current of air, the temperature sinks from 50° to 5°. Alko-

* Physical and Literary Essays of Edinburgh, vol. ii. p. 159.

hol applied in the same way sinks it to 31°, and water to 38° *. The evaporation being more rapid when the fluid is placed in a jar on the plate of the air-pump, and the air exhausted, greater cold is produced; and in this way also, as Dr Cullen observed, by the evaporation of ether, water is frozen, by adding a second receiver, over the one in which the exhaustion was performed, so as to exclude as much as possible the heating agency of the atmosphere. Dr Higgins states, that, from the evaporation of ether in this way, in frosty weather, the temperature is reduced 40° below 32° †.

Degrees of cold much more intense are obtained by the chemical action of certain substances on each other. In every case of this kind, we find that the cold is produced by the mutual action either of two solid bodies, or of a solid and a fluid, which in the progress of that action pass into the fluid state; and to this change of form the absorption of caloric, which constitutes the reduction of temperature, is no doubt to be ascribed.

The principal ingredients of these Freezing Mixtures as they are named, are substances belonging to the class of salts. In the solution of many salts in water, the temperature is considerably reduced. By adding common nitre to water, in as large a quantity as can be dissolved at a moderate temperature, that of 68° of Fahrenheit, a reduction of temperature is ob-

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* Walker on Cold, p. 82.

† Minutes of a Society for Philosophical Experiments, p. 81.

tained equal to 17 degrees; and by dissolving muriate of ammonia in water, in the same way at the same temperature, a reduction equal to 26° or 28°. Nitrate of ammonia in fine powder, added to an equal weight of water, in dissolving, reduces the temperature from 50° of Fahrenheit to 4°: and 3 parts of muriate of lime, added to 2 of water, sink it from 36° to —1°.

Mr Walker, reflecting that water, although saturated with one salt, will dissolve a portion of a second, and even of a third, was led to suppose, that by adding successively two or more salts to water, he might obtain a greater cold than from the solution of one. On making the experiment, he found this to be the fact, and by different mixtures of this kind, produced degrees of cold which were formerly not produced without the assistance of snow or ice.

One of the most powerful and convenient mixtures of this kind, is that composed of equal parts of muriate of ammonia and nitrate of potassa reduced to powder. Five parts of this mixture, added to eight parts of water at 50°, reduce the temperature to 11°. And, what renders it the most economical of these compositions, is, that by evaporation of the solution to dryness, the powder obtained answers equally as before; and in this way the same materials, when recovered for the twelfth time, had the same effect *. Six parts of nitrate of ammonia, and six of carbonate of soda, added to six of water, reduce the temperature

* Walker on the Production of Artificial Cold, p. 25.

from 50° to —7°, which is the greatest cold obtained from adding salts to water.

When salts are dissolved, not in pure water, but in acids more or less diluted, more intense colds are in general produced, no doubt owing to the solution proceeding more rapidly. Sulphate of soda, added to nitrous acid, previously diluted with 1 part of water, gives a fall of temperature from 51° to —1°; added to sulphuric acid diluted with an eqnal weight of water, the reduction is from 50° to 5°; and three parts of the salt in fine powder, with two parts of muriatic acid, reduce the temperature from 50° to 0. Other salts have similar effects. When mixed salts are added to the acids, the degrees of cold are rather greater. Phosphate of soda 9 parts, nitrate of ammonia 6 parts, and diluted nitric acid 4 parts, the most powerful of these, cause the thermometer to descend from 50° to —21°.

By a succsssive application of these mixtures of saline substances with acids, so as to reduce the temperature of the materials, Mr Walker, succeeded in freezing quicksilver *.

It has been long known, that ice or snow, added to acids, dissolves quickly, and during its solution produces a considerable degree of cold. An observation of this kind was made by Boyle, though not much attended to. Experiments on the powers of the different acids have been since made by different chemists, and by the cold thus produced, Professor Braun first suc-

* Walker on Cold, p. 35.

ceeded in freezing quicksilver, the experiment having been made at Petersburgh when the temperature of the atmosphere was low, it being necessary for the success of it with these materials, that their temperature should be at least —10° *. The cold produced by the different acids is different, and varies also according to their state of concentration. According to Mr Lowitz, when the acids are undiluted, muriatic acid produces the greatest cold, nitrous is next to it, and sulphuric acid gives the least, the first sinking the temperature from the freezing point of water to —29° of Fahrenheit, the second to —22°, and the third to —11° †. When diluted, however, the sulphuric acid exceeds the other in refrigerating power, a degree of cold equal to —78° having been produced from its action on snow at a very low natural temperature. It was found by Lowitz, that if the acids be cooled so low as to be congealed, on mixing them with snow in that state, they fail in producing the cold they produce when liquid.

From the mutual action of snow or ice and solid salts, we also obtain very great reductions of temperature. The experiments of Fahrenheit, in which he obtained the degrees of cold about that at which he commenced the scale of his thermometer, by mixing snow with sea-salt, or with muriate of ammonia, have been long known. Mr Lowitz has more particularly

* Philosophical Transactions, vol. lii. p. 156.

† *Annales de Chimie*, t. xii. p. 301.

attended to this variety of freezing mixture, and has discovered methods of producing very intense colds. The temperature of the atmosphere being 32° of Fahrenheit, a mixture of solid and dry potassa with snow, reduced the temperature to —53°. A similar mixture with soda gave a cold of only —15°. Various other saline substances gave similar low temperatures, particularly nitrate of lime, muriate of magnesia, muriate of iron, and acetite of potassa *. They were all inferior, however, in producing cold, to the pure potassa *.

Mr Lowitz, however, succeeded in discovering a salt much less expensive and less unpleasant in operating with than potassa, equally or even more effectual in producing cold,—the muriate of lime. The degree of cold produced varied according to the proportions; but the greatest was with 4 parts of the salt and 3 of snow, which, when the temperature of the atmosphere is about 5°, sink the temperature to —56° *. The addition of a little more salt did not lessen the effect, while using a smaller proportion did. To render it more certain, therefore, Lowitz recommends as the best proportions, 3 parts of the salt with 2 of snow. With such a mixture, quicksilver can be easily congealed, and Mr Lowitz, in one experiment, froze 35 pounds of it.

These experiments have been often repeated by chemists; and within these few years, the effects of

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* *Annales de Chimie*, t. xxii. p. 302—3, 305.

these intense colds, on a number of substances, have been ascertained. A series of experiments of this kind were performed by Fourcroy and Vauquelin. By mixtures of diluted acids with snow, and of muriate of lime with snow, they produced reductions of temperature to 50°, 60°, and even to 65° below the commencement of Fahrenheit's scale. A saturated solution of ammonia in water crystallized at —44°, and at —56° was converted into a semitransparent mass, and lost nearly all its odour; nitrous acid crystallized at the latter temperature; at —48° sulphuric ether became thick and milky, and at length formed a white mass, composed of small crystals; alkohol could not be congealed *.

Guyton, by transmitting ammonia in its gaseous form, and deprived as much as possible of water, into a balloon, cooled by a mixture of muriate of lime and snow, found it condensed into a fluid at —48° of the centigrade scale, or —56° of Fahrenheit †. Van Mons observes, that at these low temperatures, the most ductile metals, gold, silver and lead, lose their tenacity, and become brittle ‡.

In conducting the process of artificial refrigeration, a number of circumstances require to be attended to, in some measure varied according to the kind of freezing mixture which is employed. In obtaining cold from the solutions of salts in water, or in acids, it is necessary that the salts employed should be fresh

* *Annales de Chimie*, t. xxix. p. 281. † *Ibid.* p. 297.
‡ *Ibid.* — ——— —— p. 300.

crystallized, not efflorescent, and at the same time not damp, and reduced to fine powder; the materials ought to be quickly and accurately mixed; the vessel in which the mixture is made should be just large enough to contain it; and the vessel in which the substance designed to be subjected to refrigeration is contained, ought to be of glass, and thin. In employing mixtures of snow with acids or salts, the snow should be taken loose, dry, and if possible newly fallen; the quantities of materials should be mixed at once in their due proportion, and as quickly as possible. If muriate of lime be employed, it should be perfectly dry, and in fine powder. Lowitz directs that it should be in that state in which it is crystallized with the largest quantity of water of crystallization, which is done by putting its solution to cool, when of the density of 1.5 or 1.53; while Guyton advises, that the solution should be evaporated, until, on cooling, it form a solid mass. When pulverized in this state, it attracts a portion of humidity from the air; but the water thus attracted still becomes solid, and the powder is therefore obtained dry. The observation of Lowitz, however, that the muriate of lime produces the greatest cold, when in its perfectly crystallized state, is confirmed by Walker. In cooling the materials, where this is requisite, they ought to be put into separate glass or tin vessels, placed in a freezing mixture of the requisite power; but care must be taken not to cool them beyond that point at which they act on each other, or in other words, near to that at which the fluid resulting from their mutual action congeals. Thus, if

snow and salt are mixed at —10° of Fahrenheit, they have no action on each other; or if snow and potassa be mixed, each at —69°, they remain perfectly solid; but if the temperature be raised to —53°, their action commences, and a cold is produced of —70°. Lastly, the due proportions of the ingredients should be observed; for if there is any considerable excess of either, it merely communicates caloric to the mixture during the refrigeration, and so far diminishes the effect.

The cold produced by all these mixtures, is no doubt to be ascribed to the absorption of caloric, which attends the rapid liquefaction of the materials from their mutual chemical action, and of course is ultimately to be referred to the enlargement of capacity consequent on that change of form; the cold produced being greater as the capacity is more enlarged. This view was accordingly very distinctly presented by Dr Irvine *. Although it is no doubt the ultimate principle of the theory, there are some intermediate facts, which, for its full illustration, require to be stated.

Thus, we may in some measure predict, what substances are best fitted, by their mutual action, to produce cold,—what degree of cold may be expected from their mixture in any given case,—what will be the maximum of refrigeration,—and what will be the best proportions of the materials to obtain that maximum.

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* Essays on Chemical Subjects, p. 18.

It is obvious, *à priori*, that those substances will produce the greatest cold, which, by their mutual action, produce the most rapid solution,—which, during that solution, suffer the greatest augmentation of capacity,—and which form a solution that even at very low temperatures preserves its liquid form.

There is perhaps no individual mixture in which all these circumstances are present to the greatest extent; yet the knowledge of them enables us, in a great measure, to point out the respective powers of the different kinds of mixtures which are employed.

Thus, in the solution of a salt in water, we have merely the gradual transition of the solid to the fluid form; hence the cold produced is not considerable. When two salts are mingled together, these, by their reciprocal action, both accelerate the solution of each other, and enable a given quantity of water to dissolve a greater quantity; as more solid matter, therefore, passes to the fluid state, and passes more quickly, a greater portion of caloric may be expected to be absorbed in a given time; and accordingly a greater degree of cold is produced. The attraction of acids to water, or to speak more correctly, to the solid part of water, is strong, and their mutual action is energetic; ice too is a substance which, in its transition to fluidity, suffers a very considerable augmentation of capacity; hence from these facts it may be concluded, what experiment proves to be just, that from the action of acids on snow or ice, a great degree of cold will arise. Lastly, in the mixture of two solid substances, which by their mutual action pass to fluidity, the comparative enlargement of

capacity must be greater, and hence a greater diminution of temperature produced. It is so in fact; at the same time there is a limit placed to it, from two solids acting with greater slowness on each other, than a solid and fluid do; the transition to fluidity is from this cause more gradual, and the caloric not so rapidly absorbed. Hence we find, that the cold produced in these cases, is not equal, as Blagden observed, to the cold arising from the solution of the salt in water, added to the cold that would also arise from the sudden liquefaction of the ice. This also is the reason why the mixture of acids with snow or ice are in many cases equal to the mixtures with solid salts; because, although in the latter case more matter passes to the fluid form, yet in the former, a given quantity is liquefied more rapidly. And those salts which produce the greatest cold, are those which exert the strongest attraction to water, and act on it most rapidly, as potassa and muriate of lime.

There is another principle, however, to be attended to, which in all these mixtures modifies the quantity of caloric that is absorbed from the liquefaction. Although the indirect consequence of the chemical action between the substances mixed, is absorption of caloric, in consequence of the liquefaction it occasions, yet its direct tendency is to evolve caloric, by the increase of density which chemical action, independent of change of form, always occasions. Hence two effects result from the mutual action of the ingredients of freezing mixtures; evolution of caloric, as the immediate result of the combination, and absorption of caloric, as the re-

sult of the liquefaction to which the combination gives rise; and the ultimate effect is compounded of these, or the actual change of temperature, is only the excess of the one over the other.

In may even happen, that the one shall exactly counterbalance the other, of which we find an example in an experiment related by Mr Walker, that of the solution of sulphate of soda in alkohol, which produces neither heat nor cold; or, it may happen, that the heat from condensation shall exceed the cold from liquefaction, as in the solution of potassa in water.

The general principle I have now stated, is very distinctly exemplified in the action of acids on ice, and as applied to this case, is clearly stated by La Place: "If the mixture of an acid, with a given quantity of water, produce heat, in mixing that acid with the same quantity of ice, it will produce heat or cold, according as the heat which results from its mixture with water, is more or less considerable than that which is necessary to melt the ice *."

On this principle many of the facts connected with the operation of freezing mixtures are explained. Thus we perceive why concentrated sulphuric acid poured on snow or ice, produces at first heat instead of cold; the action is so energetic that the caloric evolved from the combination, is superior to what is absorbed by the liquefaction. But when sulphuric acid is combined with a portion of water, its affinity for more water being weakened by the quantity already combined with

* *Mémoires de l'Acad. des Sciences*, 1780, p. 392.

it, its action is less energetic, and less augmentation of temperature attends their union. Hence in the progress of the experiment in which the concentrated acid is poured on snow, although heat is at first produced, it is soon succeeded by cold, or if the acid has been previously diluted with a portion of water, it will then, when added to the snow, immediately produce cold. Even nitric acid, as Mr Cavendish observes, produces at first a degree of heat when added to snow, but when diluted with $\frac{1}{4}$ of water, it *immediately* occasions cold. The requisite dilution is, therefore, less in nitric than it is in sulphuric acid, and it is still less in muriatic, and we perceive the reason of this,—these acids evolving much less caloric when they combine with water than sulphuric acid does, and, therefore, counteracting less the cold from the liquefaction; yet even they when diluted to a certain extent, cause a greater reduction of temperature, by their mixture with snow, than when they are in a more concentrated state, though they do not bear to be diluted so much as sulphuric acid. And, lastly, if the dilution of the acid be carried too far, its attraction may be at length so much weakened, that its action on the snow will be feeble, the liquefaction will be performed slowly, and hence no great cold will be occasioned.

In the other kinds of freezing mixtures, there can be no doubt that the same circumstance operates, though perhaps to less extent. The heat from combination always counteracts the cold from liquefaction; it is only the excess that prevails, and in no case is the whole reduction of temperature that would arise from

the mere liquefaction of the quantity of matter employed, obtained. This explains to us the reason why crystallized salts produce more cold than the same salts deprived of their water of crystallization. By its presence, the mutual action of the salt and the substance mixed with it is rendered less energetic, and therefore less heat is evolved from the combination. Probably also water, in becoming liquid, may suffer a greater enlargement of capacity than a salt does; and this may have a share in increasing the refrigerating power of the crystallized salts.

From these observations, it follows, that the greatest cold will be obtained from the mixture of substances which act mutually, so as to pass most quickly into the fluid state, and which in that transition have their capacities most enlarged. But as this rapid action is the result of an energetic affinity, this may counteract, by the evolution of caloric to which it gives rise, the cold that would otherwise be produced. In all cases, therefore, there will be a certain state of concentration of the materials, and a certain proportion of them, from which the greatest cold will be obtained.

It may be remarked, too, that the quantity of cold, if the phrase may be employed, which may be obtained from a freezing mixture, is a different thing from the extent to which the reduction of temperature in the thermometrical scale may be carried; and the fact is true, that we do not obtain the most intense colds from those mixtures which, during their mutual action, absorb most caloric. If we take two freezing

mixtures at 32°, the one, for example, muriate of lime and snow, the other diluted sulphuric acid and snow, the former will produce more cold than the latter, it will sink the thermometer to —40° or —50°, while the other will sink it to not more than —25°. But we may reach a lower point in the scale of temperature, by successive application of diluted sulphuric acid and snow, than we can do by muriate of lime and snow; for, past a certain temperature, the latter mixture does not liquefy, but, on the contrary, were it liquid would become solid, while the former remains liquid at much lower temperatures than this. If we cool, previous to mixture, muriate of lime and snow to —70°, no advantage is gained; for whatever may be their temperature, they cannot produce one lower than this, or at least than —73°, as their combination cannot exist liquid at temperatures below that point; and even by approaching very closely to it before mixture, we rather diminish their mutual action, by adding to the cohesion of each. But by previously cooling diluted sulphuric acid and snow, an important advantage is gained; no limit is placed to their mutual action, and the lower the temperature is reduced, it is obvious, that the lower will the temperature be that results from their mutual action.

This furnishes us therefore with a rule by which we may determine the extreme point to which the cold, in the scale of the thermometer, from a freezing mixture may be carried. It can never exceed that point at which the liquid combination resulting from that mixture congeals or crystallizes, and must

indeed always be a degree or two above it. Thus a saturated solution of sea-salt in water, congeals at a few degrees below o of Fahrenheit; and hence the cold resulting from that salt mixed with ice or snow is never lower in temperature than this. This gives us the reason why sulphate of soda scarcely produces any cold when mixed with ice, as it lowers the freezing point of water only a few degrees, while potassa or muriate of lime produce intense colds, as they lower that point to a much greater extent.

This also, in some measure, determines the proportions in which the substances should be mixed together; those being best, in which the action shall be most rapid, without being at the same time too energetic to evolve heat from the combination; and in which the resulting solution is of that strength, that is least liable to congeal or crystallize. A little salt added to water, depresses its freezing point only a few degrees; and therefore, to add a small portion of it to snow, cannot produce much cold; while, when added until the water is saturated, that is in the proportion of 1 of salt to 5 of snow, the freezing point is lowered to —6°; and therefore, by adding it in that proportion to snow, nearly that temperature is attained. To add it in larger quantity must be superfluous, as merely adding to the matter which is to be cooled.

In the following Table, I have stated the powers of the different freezing mixtures, or the reductions of temperature which may be accomplished by the different combinations that have been employed, as they are determined by the two chemists who have made

the greatest number of experiments on this subject, Walker and Lowitz. The experiments of other chemists differ so little from these, that to state them would be to extend the table without any advantage.

TABLE OF FREEZING MIXTURES.

	Temperature reduced			
Muriate of ammonia, 5 parts, nitrate of potassa 5, water 16,	from 50°	to	10°	W.
Muriate of ammonia 5 parts, nitrate of potassa 5, sulphate of soda 8, water 16, -	50	to	4	W.
Nitrate of ammonia 1, water 1,	50	to	4	W.
Sulphate of soda 8, muriatic acid 5,	50	to	0	W.
Sulphate of soda 5, sulphuric acid diluted with an equal weight of water 4 parts, -	50	to	3	W.
Sulphate of soda 3, nitric acid diluted with an equal weight of water 2, -	50	to	3	W.
Nitrate of ammonia 1, carbonate of soda 1, water 1, - -	50	to	−7	W.
Sulphate of soda 6, muriate of ammonia 4, nitrate of potassa 2, diluted nitric acid as above, 4,	50	to	−10	W.
Phosphate of soda 9, diluted nitric acid 4, -	50	to	−12	W.
Sulphate of soda 6, nitrate of ammonia 5, diluted nitric acid 4,	50	to	−14	W.
Phosphate of soda 9, nitrate of ammonia 6, diluted nitric acid 4,	50	to	−21	W.
Muriate of soda 1, snow 2 parts,	32	to	−5	W.
Carbonate of ammonia dry, snow *,	32	to	−6	L.

* In the table of Lowitz, *Annales de Chimie*, t. xxii. p. 300. the proportions of the materials are not given, but from the context they appear to have been equal parts.

	Temperature reduced		
Nitric acid diluted, snow	from 32°	to −10°	L.
Concentrated sulphuric acid, snow,	32	to −10½	L.
Muriate of soda 2, muriate of ammonia 1, snow 5, -	32	to −12	W.
Soda crystallized, snow, -	32	to −15	L.
Potassa deprived of its water of crystallization, (lapis causticus), snow, -	32	to −15	L.
Concentrated acetous acid, snow,	32	to −17	L.
Carbonate of potassa, snow, -	32	to −17	L.
Nitrate of lime, snow, -	32	to −17	L.
Oxymuriate of antimony, snow,	32	to −17	L.
Muriate of soda 10, nitrate of potassa 5, snow 24, -	32	to −18	W.
Muriate of magnesia, snow, -	32	to −22	L.
Sulphuric acid diluted with one-half its weight of water 2 parts, snow 3 parts, - -	32	to −23	W.
Muriate of soda 5, nitrate of ammonia 5, snow 12, -	32	to −25	W.
Acetite of potassa, snow, -	32	to −26	L.
Muriate of iron, snow, -	32	to −27½	L.
Concentrated muriat. acid 5, snow 8,	32	to −27	W.
Muriatic acid and snow, -	32	to −30	L.
Concentrated nitrous acid 4, snow 7,	32	to −30	W.
Nitrous acid and snow, -	32	to −22	L.
Concentrated solution of potassa, snow, - -	32	to −30	L.
Muriate of lime 5, snow 4, -	32	to −40	W.
——— 3, —— 2, -	32	to −50	W.
——— 5, —— 3, -	32	to −53	L.
Potassa 4, snow 3, -	32	to −51	W.
	32	to −53½	L.

	Temperature reduced
Muriate of lime 2, snow 1,	from 0° to −66° W.
——— 3, —— 1,	−40 to −73 W.
Sulphuric acid diluted with half its weight water 10, snow 8,	−68 to −91 W.

Having stated every fact of importance with regard to the range of temperature, natural or artificial, I shall conclude the history of Caloric with the Table which follows, exhibiting the principal points that have been marked in the scale of heat.

	Wedg.	Fahren.
Extremity of the scale of Wedgwood's thermometer	240°	32277°
Greatest heat of an air furnace 8 inches in diameter, which neither melted nor softened Nankeen porcelain	160	21877
Chinese porcelain softened, best sort	156	21357
Cast iron thoroughly melted	150	20577
Hessian crucible melted	150	20577
Bristol porcelain not melted	135	18627
Cast iron begins to melt	130	17977
Greatest heat of a common smith's forge,	125	17327
Plate glass furnace (strongest heat)	124	17197
Bow porcelain vitrifies	121	16807
Chinese porcelain softened, infer. sort	120	16677
Flint glass furnace (strongest heat)	114	15897
Derby porcelain vitrifies	112	15637
Chelsea porcelain vitrifies	105	14727
Stone-ware baked in	102	14337
Welding heat of iron, greatest	95	13427
Worcester porcelain vitrifies	94	13297
Welding heat of iron, least	90	12777
Cream-coloured ware baked in	86	12257
Flint glass furnace (weak heat)	70	10177
Working heat of plate glass	57	8487
Delft ware baked in	41	6407
Fine gold melts,	32	5237

	Wedg.	Fahren.
Settling heat of flint glass -	294°	847°
Fine silver melts - -	28	4717
Swedish copper melts -	27	4587
Silver melts (Dr Kennedy) -	22	3937
Brass melts - -	21	3807
Heat, by which enamel colours are burnt on - - -	6	1857
Red-heat fully visible in day-light *	0	1077
Iron red-hot in the twilight, -		884
Heat of a common fire (Irvine) -		790
Iron bright red in the dark, -		752
Zinc melts, - -		700
Quicksilver boils (Irvine) -		672
——— (Dalton) -		660
——— Crichton) -		655
Lowest ignition of iron in the dark -		635
Linseed oil boils, - -		600
Lead melts (Guyton, Irvine) -		594
Sulphuric acid boils (Dalton) -		590
The surface of polished steel acquires a uniform deep blue colour - -		580
Oil of turpentine boils - -		560
Sulphur burns - -		——
Phosphorus boils - -		554
Bismuth melts (Irvine) -		476
The surface of polished steel acquires a pale straw colour - -		460
Tin melts (Crichton, Irvine) -		442
A mixture of 3 parts of tin and 2 of lead melts; also a mixture of 2 parts of tin and 1 of bismuth melts - -		334
A compound of equal parts of tin and bismuth melts - -		283
Nitric acid boils - -		242
Sulphur melts - -		226
A saturated solution of salt boils -		218

* The above, with the exception of that ascertained by Dr Kennedy, are on the authority of Wedgwood.

	Fahren.
Water boils (the barometer being at 30 inches); also a compound of 5 parts of bismuth, 3 parts of tin, and 2 parts of lead, melts	212°
A compound of 3 parts of tin, 5 of lead, and 8 of bismuth, melts rather below	210
Alkohol boils	174
Bees wax melts	142
Spermaceti melts	133
Phosphorus melts	100
Ether boils,	98
Heat of the human blood,	98
Medium temperature of the globe,	50
Ice melts	32
Milk freezes,	30
Vinegar freezes at about	28
Strong wines freeze at about	20
A mixture of 1 part of alkohol and 3 parts of water freezes	7
A mixture of alkohol and water in equal quantities freezes	—7
A mixture of 2 parts of alkohol and 1 of water freezes	—11
Melting point of quicksilver (Cavendish)	—39
Liquid ammonia crystallizes (Vauquelin)	—42
Nitric acid spec. gr. about 1.42 freezes (Cav.)	—45
Sulphuric ether congeals (Vauq.)	—47
Natural temperature observed by Mr Hutchins at Hudson's Bay,	—50
Ammoniacal gas condenses into a liq. (Guyt.)	—54
Nitrous acid freezes (Vauq.)	—56
Cold produced from diluted sulphuric acid and snow, the materials being at the temperature of —57	—78½
Greatest artificial cold yet measured (Walker)	—91

CHAP. II.

OF LIGHT.

LIGHT, like Caloric, is an agent too subtle to admit of its combinations being acourately traced. We know that it exists in some substances as a constituent principle, since it is disengaged from them when they enter into new combinations; but we are unable to obtain, in a separate state, the bases with which it was combined. In its chemical history, therefore, we can state only the effects it produces, the circumstances connected with its absorption and evolution, and the results of the researches that have been made with regard to its nature and constitution.

The materiality of this agent is sufficiently proved. Its motion, though inconceivably rapid, is progressive, and may be measured; it may be stopt in its progress, or its direction may be changed; it may be condensed into a smaller or dispersed over a larger space; it is inflected when passing near to any body, which proves it to be subject to gravitation; and it produces chemical changes in many bodies, which show that it is equally subject to chemical attraction. It exists in them in a state of combination, and is disengaged by

the exertion of new affinities, when it appears in its original form.

Two opinions have been maintained with regard to the nature of Light, both admitting its materiality. Descartes and Huyghens supposed that the phenomena it presents arise from vibrations propagated through an extremely rare and elastic fluid, which is diffused through all space, and in which fluid luminous bodies have the power of exciting these vibratory motions, as sonorous bodies have the power of exciting vibrations in the air,—an hypothesis which Euler afterwards embraced. Newton, on the contrary, regarded light as an emanation of particles of extreme minuteness, projected in right lines from the sun, and from all luminous bodies, and moving with extreme velocity. The opinion of Newton has been generally received. It accords better than the other with the phenomena of optics, and appears to be established by the chemical agencies which light exerts, its fixation in bodies, and its subsequent evolution.

If this opinion be received, it is obvious that the minuteness of the particles of light must be astonishingly great, and the imagination requires even some aid to be able to form any conception of it. "There is no physical point," says Melville, "in the visible horizon, which does not send rays to every other point; no star in the heavens which does not send light to every other star. The whole horizon is filled with a sphere of rays from every point in it, and the whole visible universe with a sphere of rays from every star. In short, for any thing we know, there

are rays of light joining every two physical points in the universe, and that in contrary directions, except where opaque bodies intervene." How great, then, must be the subtilty of these particles, to prevent their interrupting each other; and at what an immense distance must each particle in a ray be placed? This will be apparent, if we consider the course of a ray of light from any of the remoter fixed stars to the human eye. When projected, it first passes through the surrounding space, in which are probably several planets revolving, and which must therefore be filled with a sphere of rays from each of them; in every part of the intermediate space between that star and our solar system, it has passed through rays of light flowing in all directions from every fixed star in the universe; and lastly, in reaching this earth, it has passed across the whole ocean of the solar light, and also that light which is emitted from the planets, satellites, and comets. Yet in this course its progress has not been interrupted.

The minuteness of the particles of light may also be estimated by the velocity with which they move. From astronomical observations, it appears that light moves at the rate of at least 164,000 miles in a second; a particle of light projected from the sun arriving at the earth in about $8\frac{1}{4}$ minutes. Were not its particles inconceivably minute, their momentum, arising from such velocity of motion, must be such as to destroy every substance on which they impinge. Yet it is doubtful whether the momentum they do possess is such as to be capable of being ascertained by the most

delicate mechanical contrivance. From an experiment of this kind, it has been calculated that the quantity of matter in the rays of light collected by a concave mirror, of two feet in diameter, would not amount to more than one twelve hundred millionth part of a grain; and how many particles of light must have been in these accumulated rays?

The particles of light, like those of caloric, appear to repel each other. So perfect is its elasticity, that it is reflected from a body at an angle, equal to the angle of its incidence. It is subject to that attraction which is exerted between masses of matter, as, when passing near to a body, it is inflected towards it; and in passing obliquely from one medium into another, it is turned from the direct course in which it was proceeding. If it pass from a more rare into a denser medium, it is bent towards the perpendicular; if from a denser to a rarer medium, the reverse, the degree in which this takes place being different, according to the density and the nature of the medium. This is named the refraction of light.

Newton made the capital discovery, that a ray of light is not homogeneous, but consists of various rays, which being differently refrangible, are separated from each other when an entire ray of light is made to fall on a refracting medium at a great angle of incidence. By thus passing a ray of white light through a triangular glass prism, it is divided into seven rays, distinguished by different colours, red, orange, yellow, green, blue, indigo and violet, which, however, are not perfectly well defined, each passing insensibly into

the contiguous one. Of these the red is the least refrangible, and therefore falls on a space least distant from that which the entire ray of light would have fallen on, had it passed through the prism without decomposition, or without having its direction changed. The violet is the most refrangible, it therefore is at the greatest distance; these two bounding the space which the rays occupy, or the prismatic spectrum as it is termed, the others being arranged in the order above stated, and occupying unequal spaces in the spectrum. By separating each of these rays, and again transmitting it through a prism, it is refracted, but without suffering any farther change.

These rays differ not only in refrangibility, but in their other properties. Dr Herschel has shewn that their illuminating powers are very unequal. By employing the microscope, and causing the different coloured rays to fall successively on an object under it, he found "with respect to the illuminating power assigned to each colour, that the red making rays are very far from having it in any eminent degree. The orange possess more of it than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is nearly equally bright with the yellow; but from the full deep green, the illuminating power decreases very sensibly. That of the blue is nearly upon a par with that of the red; the indigo has much less than the blue; and the violet

is very deficient *." These rays have also different chemical powers.

The differences in the coloured rays, so far as they were known to Newton, were supposed by him to depend on the different magnitudes of their particles, the red being supposed to consist of particles of the largest size. By others they have been ascribed to the different velocities with which they are projected from the luminous body; the red moving, it is supposed, with the greatest, the violet with the least. With whatever probability these hypotheses may explain optical phenomena, they scarcely afford an explanation of the fact that these rays differ not only in their mechanical properties, and in the sensations of vision which they excite, but likewise in their chemical powers.

The rays of light have different relations to different bodies. Through some they pass with scarcely any interruption: these are named transparent, or diaphanous, and, according to Newton, consist of particles which are arranged with uniformity, and are of equal density, so that the ray of light meets with no obstacle, and is not attracted from its course. By some bodies the greater part of the rays which fall on their surface are immediately reflected. Some reflect one ray retaining the others, which gives rise to the different colours bodies exhibit; and lastly, there are some by which the light is absorbed, and in which, by numerous reflections and refractions in their pores, it is lost, constituting blackness.

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* Philosophical Transactions for 1800, p. 267.

Light can also form a more intimate union with bodies, and be retained in them by a stronger attraction. Of this there appear to be different degrees. In many cases it is absorbed without producing any change in the sensible qualities of the body, and is again slowly given out: in others it occasions alterations of temperature and of composition, or acts as an important chemical power.

The first of these cases constitutes Phosphorescence. There are a number of substances which, on being exposed to the solar rays, appear luminous when removed to a dark place, and continue to emit light, some for a longer, others for a shorter time. The luminous appearance becomes, however, gradually fainter in all of them, and at length ceases, but it is renewed without any abatement by exposing them again to the light of the sun. The bodies possessing this property are termed Phosphori, or Solar Phosphori, to distinguish them from an inflammable substance, named Phosphorus, which is of a quite different nature.

This phosphorescent property was first observed in a fossil termed the Bolognian Stone (a natural sulphate of barytes). Margraaf, Du Fay, and others, discovered a number of other substances which possessed the same quality in a greater or less degree, and Beccaria and Wilson found that almost every kind of matter in a solid state, the metals and a few other bodies excepted, might be made to emit light, by being exposed to the solar rays.

There is, however, a very great difference among these bodies, in the quantity of light which they emit,

under the same circumstances. The shells of marine animals, the bones of land animals, some of the gems, marbles, limestone, sulphate of barytes, fluor spar, and other combinations of earths with acids, are the most powerful natural phosphori;—sugar, white paper, and linen, possess the same quality in an eminent degree. In general white bodies are more powerfully phosphorescent than those of a dark colour, though to this there are many exceptions, and there are some very white which possess scarcely any of this property.

Artificial solar phosphori may be prepared, which emit much more light, and for a longer time than the natural phosphori. Of this kind is the Bolognian phosphorus, the substance which was first discovered to possess this property. The Bolognian stone is merely a sulphate of barytes. Any variety of this fossil that is pure answers the purpose equally well. A quantity of it is made red hot in a crucible, and is reduced to a very fine powder in a stone or glass mortar (a metallic one being absolutely unfit). This powder is made into a paste with mucilage of tragacanth, and divided into thin cakes, which are to be dried with a gentle heat, gradually increased. A furnace is then to be filled with pieces of charcoal to three-fourths of its height, and the fire kindled. Upon this are laid the flat cakes, and more charcoal is placed over them so as to fill the furnace. The fire is to be continued till all the fuel is consumed; the cakes are then to be cleaned from the ashes by blowing on them with bellows. They are to be kept excluded from the air. When exposed for a minute or two to the open air in a clear light, they ap-

pear luminous when removed to the dark, and their luminous appearance is even greater than when they have been exposed to the solar rays, the heat in the latter case causing the light to be very rapidly emitted.

Another artificial solar phosphorus is that termed Baldwin's. It is nitrate of lime which has been exposed to a red heat in an earthen vessel. Its phosphoresence is much inferior to that of the former.

The most powerful of the artificial solar phosphori is that termed Canton's, which is a sulphuret of lime. To prepare it, oyster-shells, freed from their impurities by washing, are exposed to a red heat in a common fire for half an hour; the purest part is separated and powdered in a stone mortar. Three parts of this powder are mixed with one of sulphur; this mixture is pressed close down into a crucible till it be almost full; it is placed in the middle of a fire, and kept red hot for one hour at least. When it is cold the mass is broken, and the whitest parts scraped off for use *. Or what is recommended in preference to this by Dr Higgins, the oyster-shells, after being calcined without being reduced to powder, are to be put into the crucible in alternate layers with sulphur, and exposed to the requisite heat.

This phosphorus, after it has been exposed for a few seconds on the outside of a window to the common light of the day, appears very luminous in a dark place. The figures on the dial-plate of a watch may be distinguished by its light.

* Philosophical Transactions, vol. lviii. p. 337.

The phosphorescent property in all these bodies appears to be the same, differing only in degree. Those which are weak require to be exposed to the solar rays to render them luminous, and some even to the rays concentrated by a lens. With regard to the stronger phosphori, it is sufficient to expose them to clear daylight for one or two minutes; after this exposure they are equally luminous as when they have been exposed to the light of the sun, and they continue longer so, as in the latter case the heat which they at the same time receive contributes to expel the light more rapidly. Some can be illuminated by the light of a candle or by that of an Argand's lamp concentrated by a mirror. The light of the moon, or that emitted from other phosphori is insufficient. The exposure of a few seconds to the light is sufficient to illuminate them, and when they are exposed for a longer time they are not rendered more luminous. Canton's phosphorus is rendered equally luminous by passing over it an electrical discharge. The light emitted is often yellow or red, more generally it is white.

The state of these phosphorescent bodies, with respect to temperature, has a very material influence on their property of emitting light. It is extinguished by the cold of a freezing mixture, but returns as the temperature rises. If heat is communicated, the luminous appearance is greater than it would otherwise be. Beccaria proved this by a very decisive experiment. He filled a glass tube with powdered Bolognian phosphorus, and after exposing it to the light, plunged one half of it in warm water, and observed that it gave

light more copiously than the part which was in the open air. When a piece of these phosphori has ceased to emit light, it may be rendered luminous by heating it, as, for instance, by plunging it in warm water. When the luminous appearance is thus promoted by heat, it ceases however proportionally sooner. Mr Canton filled two glass-balls with his phosphorus; illuminated them at the same time, and to the same degree: both were brought into a dark room, and one of them was put into a bason of boiling water; the phosphorus in it shone much brighter than in the other, but in ten minutes it became quite dark, whereas the other continued visible for two hours after; and even then the heat of the hand rendered it more luminous. When by exposure to a certain degree of heat the phosphorescent body has ceased to be luminous, if kept in darkness it gives out no more light by that degree of heat, but it may be made to give out light by exposing it to a still higher temperature. By a temperature somewhat below ignition, Canton's phosphorus, which had been kept in darkness more than six months, gave a considerable light.

These facts, and the general phenomena of phosphorescence, evidently lead to the opinion that the phosphorescent body exposed to the light absorbs part of it, different bodies absorbing different quantities; that this light is again gradually emitted; and that its expulsion is rendered more quick by the action of caloric.

There is, however, an objection to this theory. Beccaria, on exposing pieces of solar phosphori to the light transmitted through coloured glasses, affirmed, that the

same light was again given out, that if the light, for instance, had been transmitted through a red coloured glass, the phosphorus on being removed from under it gave out a red light *. Experiments of the same nature had been long before made by Du Fay †, but with the opposite result; the light emitted not having the least tint of the colour of the glass through which it had been transmitted. They were repeated by Mr Wilson: he could not discover any difference in the kind of light emitted by the phosphorescent body, from such an arrangement; and Beccaria himself afterwards admitted, that he had been deceived. Whether the light be transmitted through coloured glasses, or what is a more unexceptionable mode of conducting the experiment, when the different rays are separated by the prism, and thrown upon the phosphorescent body, it still emits the same light which it does upon merely exposing it to the light of day. If a piece, for instance, which in the dark gives a white light, have a red light thrown upon it, or be exposed to the different rays, it still continues to give out an uniform white light: or if a piece of phosphorus, which naturally exhibits the prismatic colours, as some do, be exposed to a white light, or to any particular ray, its prismatic appearance still remains the same ‡. Nay, what is still more singular, when a specimen is selected which shines with a particular colour, red for example, if the red ray be

* Philosoph. Trans. vol. lxi. p. 212.

† *Memoires de l'Acad. des Sciences*, 1735, p. 493.

‡ Wilson's Experiments on Phosphori.

thrown upon it, it shines, according to Wilson, very feebly, while exposed to a different ray, as the violet, it gives its usual red light brilliantly; with the blue, the same, but not so vividly; and with the green less. And, on the contrary, if a piece was selected, which shone with a blue light, it was feebly excited by the blue ray, but strongly by the red *. These facts are unfavourable to the conclusion, that the light which phosphorescent bodies emit, is that which they had previously absorbed, and have led some to infer that they shine by their own native light, and that exposure to light is only necessary to excite this, and cause it to be thrown off. It is not improbable, however, that the different varieties of light are convertible into each other, and on this supposition the fact may be accounted for, in conformity with the common theory of phosphorescence.

The phosphorescent property is entirely independent of any action of the air, as any of these bodies is equally luminous for any length of time, when kept in water or in a glass vessel hermetically sealed. The phosphorescence is even impaired by long exposure to the air, though this is rather to be ascribed to the moisture of the atmosphere, than to the action of the air itself. When the phosphorescent matter is included in a glass vessel, hermetically sealed, Mr Canton has shewn, that the property remains unimpaired for a long time, (four years), the luminous appearance being produced as at first by exposure to light; but if a little water be

* *Journ. Physiq.* t. xv. p. 93.

included with it, it is soon entirely lost. Alkohol impaired it very little, and ether not at all *.

Mr Canton has justly remarked, that the phenomena which this kind of phosphorescence present, are favourable to the Newtonian theory of light, and adverse to that maintained by Euler: "That a substance should either give light or not, when its parts are agitated by the same degree of heat, according as it has or has not been exposed to light for a few seconds of time, more than six months before, seems plainly to indicate a strong attraction between that substance and the particles of light." It is certainly incompatible with the opinion of illumination depending on vibration.

There is another class of phosphorescent bodies which give out light when heated, independent of any previous exposure to light of any kind; this property is much diminished at each time the light is emitted, and is not renewed by exposure to the sun's rays. It is equally, however, with the other species of phosphorescence, independent of the action of the air. The mode of shewing this phosphorescence, is to throw a small quantity of the body, reduced to powder, on a plate of iron, heated nearly to redness, or to drop it into any hot fluid, as water or oil. In some the light is momentary; in others it lasts for several minutes: it is in general uncoloured, though, from various bodies, it is also of various colours. Fluor spar is the most powerful phosphorescent body of this family; it emits a

* Philosoph. Trans. vol. lviii. p. 339. 342.

beautiful purple light. Next to it are different marbles, feldspar, quartz, gems, and other earthy fossils; metals are much inferior, but even these give out more light in this way, than various solar phosphori such as paper, sugar, and different salts. The luminous appearance is of the same intensity, when they are heated in the exhausted receiver of an air-pump, or in different gases. Even liquids have the same light when poured on a hot iron, particularly those of an oily nature, as Brugnatelli has observed.

Attrition also excites phosphorescence in some bodies. It has been long known, that some of the gems when rubbbed shine brightly. Two pieces of quartz rubbed against each other become luminous on the surface. And in some of the fossils, as the tremolite, the phosphorescent property has been found so great, that the friction from a feather is sufficient to excite it.

Mr Wedgwood, by whom a number of experiments was made on the phospherescence from heat and from attrition *, found, that if the attrition is strong, the light emitted is much greater. By applying a piece of agate to the circumference of a wheel of grit, on causing it to revolve at a moderate rate, the agate where it touches the stone becomes red hot; if the wheel revolve at a quicker rate, the touching point emits a pure white light and glowing sparks; rock crystal, glass, and other bodies, are in the same way rendered equally luminous. In general, colourless and transparent bodies, whose surfaces become rough

* Philosophical Transactions for 1792.

by rubbing, give most light. The light is from some bodies colourless, and from others coloured of various shades. It is equally bright in the different kinds of air, and even under water. Mr Wedgwood shewed also that it is not electrical, as on rubbing two pieces of quartz together, and applying them to the fine down of a feather, the down is not sensibly affected. He supposes, that attrition excites phosphorescence entirely by the heat it occasions; this heat is momentary, and confined to the rubbed surface, but it may be sufficiently high to produce the phosphorescent appearance. An experiment has been stated by Mr Davy, which is unfavourable to this hypothesis, That if fluor-spar, as well as some other bodies, be heated until they are no longer phosphorescent on a fresh application of heat, they still give light by collision. Bournon has observed, too, that there are fossils which are rendered phosphorescent only by friction, as quartz or corundum; others only by heat, as carbonate of strontites, or of barytes, while there are many which become phosphorescent from either cause, as phosphate, fluate, and many varieties of carbonate of lime *. The very slight friction, also, which is sufficient to render some bodies highly luminous. is a fact inconsistent with the opinion of the evolution of the light being owing to the heat which attrition excites.

A light, analogous somewhat to phosphorescence, is produced in some bodies by chemical action. It is observed, when magnesia, or lime, or pure potash, is

* Nicholson's Journal, Oct. 2. p. 290.

thrown into the mineral acids, as well as in the rapid slaking of quicklime by the affusion of water *. Dizé has shewn, that it is accompanied with a considerable elevation of temperature †.

There remains to be noticed one other kind of phosphorescence, that which is exhibited by animal matter, either in a living or dead state. Marine animals are remarkable for this property, almost every kind of marine fish, after having been removed a short time from the water, being more or less luminous in the dark, and some of them shining with great brightness even for three or four days. The flesh of some quadrupeds has likewise been observed to emit light; and a similar light is afforded by certain vegetable substances, as by decayed wood, or peat-earth.

This species of phosphorescence had been made the subject of experiment by Boyle ‡, afterwards by Mr Canton ||, and more recently by Dr Hulme §. The principal facts with regard to it have thus been ascertained.

This light does not appear, unless in a few instances, until the animal has been for some time deprived of life; it is always apparent, however, before there are any signs of putrefaction. A certain degree of putrefaction does not seem incompatible with it, as ap-

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* *Mémoires de Chimie de Pelletier*, t. i. p. 35.

† *Journal de Physique*, t. xlix. p. 177.

‡ Boyle's Works, vol. iii. p. 157.

|| Philosophical Transactions, vol. lix. p. 446.

§ Ibid. for 1800.

pears from the experiments of Mr Canton; but, according to Dr Hulme, "as soon as a great degree of putrescence has taken place, the luminous property of the fishes is destroyed, and the light extinguished." He has also remarked, that in the instances recorded of the flesh of land animals being phosphorescent, it appears to have been always in a fresh state.

The luminous matter of these substances may be separated from them, and preserved for a time by certain processes. Canton observed, that sea-water, or a solution of salt prepared artificially of a certain strength, became luminous, from the substance of a fresh herring having been immersed in it. Dr Hulme found, that other saline solutions acted as solvents of this luminous matter. About four drachms of the substance of a fresh herring were put into a solution of 2 drachms of sulphate of magnesia in 2 ounces of cold water. On examining the liquor the second evening after, a lucid ring was perceived floating at the top, and on shaking the phial the whole fluid became beautifully luminous. It continued to possess this property for some time, the luminous matter separating, and being capable of being again mixed by agitation; it gradually, however, became less luminous, and on the fourth night was extinguished.

Many other saline solutions, such as those of sea-salt, of nitre, or of sulphate of soda, &c. have the same property of extracting the luminous matter from various marine animals. It is probably from the sea-water having dissolved this luminous matter that the ocean appears occasionally luminous in the dark,

though this appearance seems also to depend occasionally on other causes, especially on the presence of phosphorescent animalculæ *. Fresh-water is incapable of extracting this luminous matter, and even prevents the fish immersed in it from becoming luminous. A number of substances have the property of extinguishing this light, such as pure water, the acids and alkalies, fermented liquors, and ardent spirits; and what is singular, it is extinguished by saturated solutions of the very salts that preserve it when in dilute solutions. Dr Hulme found, however, that in these concentrated solutions the light still exists, and may be made to appear by dilution with a sufficient quantity of water, and it may thus be repeatedly extinguished and revived, by adding either salt or water.

The luminous appearance is augmented by motion or agitation; it is impaired, and even extinguished by cold, but is revived, and even rendered brighter by a moderate heat. By a great degree of heat, however, such as that of boiling water, it is immediately extinguished, and does not revive on cooling. It appears to be in some measure dependent on exposure to air, as Dr Hulme found that the parts of fish which were not thus exposed were dark, while the parts exposed were luminous. The luminous appearance, according to Dr Hulme's experiments, is not greater in oxygen gas than in atmospheric air. Though nitrogen gas appears to prevent the animal matter from becoming lumi-

* Letter by Professor Mitchell, Phil. Mag. vol. x. p. 20.

nous, it does not extinguish it when it has previously begun to shine; hydrogen gas, nitrous gas, carbonic acid gas, and sulphuretted hydrogen gas, not only prevent the luminous appearance, but extinguish it if it had come on. It is also impaired, and at length nearly extinguished in the vacuum of an air-pump, but reappears when the air is admitted *.

The emission of light in any of these cases, is not accompanied with any sensible extrication of caloric, the temperature of the luminous matter being the same with that of the surrounding air.

The light from rotten wood appears to be somewhat similar in the laws it observes. Boyle observed that a piece of rotten wood that was luminous, when it was placed in a receiver from which the air was extracted, ceased to shine, and became luminous when the air was again admitted †. This has been since confirmed by Dr Hulme. It has also been ascertained by Spallanzani, Carradori, Humboldt, and more lately by Dr Hulme and by Bockman, that, introduced into the non-respirable gases, nitrogen, hydrogen, carbonic acid, carburetted and sulphuretted hydrogen, its luminous appearance is in a short time extinguished, but is revived when atmospheric air is admitted. Dr Hulme ascertained, too, that luminous wood had the property of shining only when it had been exposed to the air, (or perhaps to the light), and that when newly broken the internal surface did not begin to shine for

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* Philosophical Transactions for 1800.

† Boyle's Works, vol. iii. p. 159.

some time. These facts appear to prove that the emission of the light depends on some action of the air, or rather of its oxygen. There are others, however, inconsistent with that supposition. Boyle relates, that a piece of rotten wood being inclosed in a glass tube which was hermetically sealed, it continued to shine as before *. And Forster mentions, that luminous wood does not change its appearance when introduced into oxygen, which is confirmed also by Hulme and Bockman. And the last experimenter ascertained, that when the luminous appearance had ceased in these gases, a fresh piece of wood shone for some time †; and likewise, that the wood when luminous continued to shine for a number of hours in spring water, or in boiled or distilled water, as well as in several saline solutions, and in linseed oil ‡. The luminous appearance was extinguished instantaneously by the acids, and speedily by alkohol, as also by a high temperature, though by a moderate heat, as that of 100°, it is rendered more vivid, while by cold it is repressed. In these circumstances, this variety of phosphorescence is similar to that of animal matter.

Certain insects, both alive and in a dead state, emit occasionally large quantities of light. The glow-worm (lampyris splendidula), has been long known for possessing this property; the light is variable, being at one moment brilliant, and at another weak or

* Boyle's Works, vol. iii. p. 180.

† Philosophical Magazine, vol. xvi. p. 22.

‡ Ibid. vol. xvi. p. 147.

extinct. It proceeds from two rings at the inferior part of the abdomen, the phosphorescent matter being included in a receptacle from which it may be expressed. Other insects have a similar phosphorescent property, as the lantern-fly of the West Indies.

Experiments on this kind of phosphorescent light have been made, principally on the glow-worm. Forster made the observation, that when the insect is placed in oxygen gas, it shines with much more splendour than it does in atmospheric air, and the brilliancy of it is also more permanent. After being removed from the oxygen, it retained the highly luminous appearance for a few minutes, but it returned soon to its usual state. The oxygen gas did not appear to be sensibly impaired in its purity. Forster conceived the luminous matter to be a secretion from the animal, connected with its respiration, and shining more when the air is inspired than when it is expired; whence he explains its variable light *. According to Carradori †, the luminous appearance depends entirely on the will of the animal. The phosphorescent matter may be obtained from its receptacle by compression; it continues to shine for a few hours, but then becomes extinct. It shines also in oil or in water, as well as in the air, and likewise in the Torricellian vacuum. The animal itself shines when immersed in water, and with more splendour in tepid than in cold water. Its shining, according to For-

* *Journal de Physique*, t. xxiii. p. 24.

† *Annales de Chimie*, t. xxvi. p. 96.

ster's observation, more vividly in oxygen gas, Carradori supposes owing merely to the stimulus which the gas communicates to the animal; and Forster indeed remarked, that the animal was more alert in oxygen than in atmospheric air.

The experiment has been repeated by Dr Hulme, and he has not found that the glow-worm, either dead or alive, shone with more splendour in oxygen gas than it does in atmospheric air. The experiment, however, appears to have been made only once on the animal while alive. Dr Hulme likewise found that this species of phosphorescence agrees with the others, in being extinguished by hydrogen, carbonic acid, sulphureted hydrogen, and nitrous gases, and returning when the animal is removed to the atmospheric air. These last experiments were made on the dead insect.

The next general fact to be noticed in the chemical history of light, is its power of producing heat. This property is sufficiently obvious. The action of the solar rays is the great source of the heat of our globe, and, when concentrated by a mirror or lens, affords nearly the most intense heat we can command.

Different substances are very unequally heated by the rays of light; transparent bodies allowing them to pass through with little interruption, are comparatively little heated, especially if of no great thickness; for Macquer long ago observed, that a piece of thick transparent glass is melted much more easily in the focus of a burning mirror, than a thin piece; and that a plate as thin as paper, which could be melted

in the flame of a candle, was not even softened in the focus of a mirror in which iron was fused *. White coloured substances are much less heated than those which are of a dark shade. Franklin, by laying pieces of cloth of different colours on snow, while the sun shone upon it, found that the darker-coloured cloths were most heated, as was rendered evident by their sinking deepest in the snow. Mr Davy made an experiment of a similar kind. He exposed to the rays of the sun, six similar pieces of copper, of equal weight size and density, coloured, one white, one yellow, one red, one green, one blue, and one black. A portion of a mixture of oil and wax, which became fluid at 76°, was attached to the inferior surface of each, and the superior surface was exposed to the rays of the sun. That on the black plate began to melt first; next the blue; then the green and the red, and lastly the yellow; that on the white plate was scarcely affected when that on the black was in a complete state of fusion †. A thermometer blackened and exposed to light, rises always higher than a thermometer of the same delicacy, the bulb of which is clean.

In giving the history of Radiant Caloric, I have related the discovery made by Herschel, that the different rays of light possess very different heating powers. Dr Hutton had formed a conclusion of this kind, probably from some imperfect observation or experiment. "The compound light," says he, "which is

* Chemical Dictionary, article "Fire."

† Beddoes' Medical Contributions, p. 44.

white, has a greater power of giving vision, in proportion to its power of exciting heat; whereas, in the red species it is the opposite; for here the power of exciting heat is greater, in proportion to its power of giving vision *." But it had never been established, until Dr Herschel began his investigation of the nature of the solar ray. Having employed different coloured glasses, in viewing the sun, he observed that in using some of them he felt a sensation of heat, though with little light, while others gave much light with scarcely any sensation of heat. It occurred to him, therefore, that the prismatic rays might have the power of heating bodies very unequally distributed among them, and this led to a series of experiments, by which the conjecture was fully demonstrated.

In a piece of pasteboard, mounted on a frame so as to be moveable, an opening was cut, a little larger than the ball of a thermometer, and of a sufficient length to let the whole extent of one of the prismatic colours pass through. A prism being placed at right angles to the solar ray, and turned until its refracted coloured spectrum became stationary, the moveable frame with the pasteboard was adjusted so as to be perpendicular to the rays coming from the prism; and beneath were placed very delicate mercurial thermometers, which could be more or less advanced, so that one only of the prismatic coloured rays should fall on the bulb.

* Dissertation on Light and Heat, p. 38.

The different heating powers of the different rays were thus ascertained, and were as follow : The thermometer rose in the red ray in ten minutes, 7° of Fahrenheit ; in the green ray, the rise in the same time amounted only to $3^{\circ}\frac{1}{2}$; and in the violet ray, in the same time likewise, to 2 degrees *.

In the prosecution of these experiments, it was found, as I have already remarked, that the heating power extended beyond the visible spectrum on the side of the red ray, and that, half an inch beyond it, the thermometer rose in ten minutes $6\frac{1}{2}$ degrees ; the heating power being greatest at about this point ; one inch beyond the visible light of the red ray, the thermometer rose in thirteen minutes $5\frac{1}{4}$ degrees, and the heating power was discoverable to the extent even of $1\frac{1}{2}$ inch †. Beyond the violet ray on the other side of the spectrum, there was no heating power.

Since the calorific rays thus occupy a larger space than the visible rays, they must be of a more extensive refrangibility. It follows also, that when the solar rays are concentrated by a lens, the focus of the rays of heat must be different from the focus of the rays of light. On making the experiment, Herschel found reason to conclude that the focus of heat was farther removed from the lens than that of light, and probably not less than $\frac{1}{4}$ of an inch ‡.

These experiments have been repeated and confirm-

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* Philosophical Transactions for 1800, p. 258—9.

† Ibid. p. 286—7.

‡ Ibid. p. 444.

ed by those of Sir H. C. Englefield, made with a differently arranged apparatus, so as to guard against the thermometers being affected by any foreign heat reflected from any part of it. A prism was placed in the proper position, in an open window; the coloured spectrum from it was thrown on a lens of 4 inches in diameter, and about 22 inches focal length. The lens, as well as its mounting, was covered with a thick white pasteboard skreen, in which was cut a slit of 3 inches long, and half an inch wide over the centre of the lens, and through which any of the prismatic colours could be transmitted, while the others were excluded. A sensible mercurial thermometer, with a naked bulb, was placed so that the bulb was in the focus of the lens, and the coloured rays were successively thrown on the slit in the skreen covering the lens, and of course on the bulb of the thermometer. The rise was as follows:

In the blue, in -	3′	from 55° to 56°
— — green, in -	3′	from 54 to 58
— — yellow, in	3′	from 56 to 62
— — full red, in	2½′	from 56 to 72
— — confines of the red,	2½′	from 58 to 73½
Quite out of visible light,	2½′	from 61 to 79

These denote the greatest effect of the different rays, as the thermometer, in all the experiments, was continued in the focus long after it had ceased to rise. When the bulb of the thermometer was blackened, the rise was much greater, rising in the full red ray in 3′ from 66° to 82°; in another experiment, to 87°,

while in the invisible ray it rose to 98º *. It was remarked in these experiments, that when the spectrum was received on the skreen covering the lens, on removing the utmost edge of the red rays, a full eighth of an inch from the edge of the slit in the skreen, there was a faint blush of red of a semi-oval form, visible when the focus of the lens was thrown on a white skreen. It was in this place, and not in the full red light, that the greatest heat was discovered, and half an inch beyond the edge of the red ray, and where there was no illumination whatever in the focus, the heat was still greater than in the red ray itself, the rise in the former being in 3′ from 69° to 79° ½, in the latter, in 3′, from 67° to 71° ½.

The experiments of Herschel, confirmed by those of Englefield, therefore prove not only that the solar ray consists of rays of visible light, but likewise of rays of radiant caloric; and it follows from them, that the heating power of the solar rays does not depend on the rays of visible light, but on the rays of radiant caloric, which being of different refrangibilities, and of a more extensive refrangibility than the rays of light, are spread over and beyond the visible prismatic spectrum. Where this matter is most completely separated from visible light, and where indeed there is no illumination whatever, the heating power is about its maximum; and as this is receded from, it diminishes, until at the other extremity of the spectrum it is extremely weak. That the heating

* Journals of the Royal Institution, vol. i. p. 203.

power which does appear to be exerted by the different visible rays, is not a property belonging to them as light, but is owing to the intermixture of rays of caloric, has been proved by Dr Herschel, and proved in a more decisive manner than the nature of the subject appeared to admit.

It may even be inferred from the phenomena that have been described. It is proved that the solar rays consist of rays of caloric and rays of light. The former, separated from the latter, are found to have a highly heating power; that power, in the entire ray, must therefore, in part at least, be ascribed, not to the visible light, but to this invisible calorific matter. It may, as well as visible light, consist of rays of unequal refrangibility, and may therefore, from this cause, be intermixed with the prismatic rays, and give them their heating power. We have no proof that light, free from this calorific matter, is possessed of this power, and we find, that the more completely they are separated, or the farther we recede from the point of the prismatic spectrum, where the calorific rays are accumulated, the less heat is produced by the visible rays of light. Do not these considerations render extremely probable the conclusion, that the remaining heating power of these rays is still owing to rays of caloric mingled with them?

The opposite conclusion, as Dr Herschel has remarked, is attended with some arbitrary and revolting positions. The illuminating power, the peculiar character of light, he has proved, is greatest towards the middle of the spectrum; from this it decreases towards

each side, and on one side it is accompanied with an increase, on the other with a decrease of heating power. It must therefore be maintained, " that a set of rays conveying heat, should all at once, in a certain part of the spectrum, begin to give a small degree of light; that this newly acquired power of illumination, should increase, while the power of heating is on the decline; that when the illuminating principle is come to a maximum, it should in its turn also decline very rapidly, and vanish at the same time with the power of heating. How can effects that are so opposite be ascribed to the same cause? first of all, heat without light; next to this, decreasing heat, but increasing light; then again, decreasing heat and decreasing light." On the hypothesis that the heating power of the visible rays is owing to the intermixture of rays of radiant caloric, of unequal refrangibility, we are pressed with no such inconsistencies.

It rests not, however, merely on these general grounds, but is established by other experiments. It is evident, that the coloured ray, if its heating power be a property belonging to it as such, and not owing to any foreign calorific matter, when transmitted through any transparent medium, should have its heating and illuminating power equally diminished. We are not to expect, that it will pass through with its powers undiminished, for we know, that in such an experiment, a loss of rays is always sustained. But we may fairly expect, that if the heating and illuminating power depend on the same matter, whatever portion of this

matter be retained, these powers must necessarily be diminished in precisely the same proportion; so that if half of the rays be stopped, both powers shall be diminished one-half, and so on in proportion; while, if the heating and illuminating powers do not depend on the same matter,—if the former depend on rays of caloric, and the latter on rays of light,—it may happen, and may even be expected, that these will be unequally acted on by the medium through which they are transmitted; one may be retained in larger quantity than the other, and hence the heating and illuminating powers will not by such transmission be diminished in the same proportion. Now, it has been established by Dr Herschel, from a very extensive series of experiments, on transmission through different kinds of glass, different coloured glasses, and different fluids, that they are not proportionally diminished, but that in some cases the illuminating is more diminished than the heating power, and in other cases the reverse happens.

Without entering on a detail of these experiments, which are numerous and complicated in their relations, some of those selected by Dr Herschel himself may be stated. Thus he remarks, that of 1000 incident rays, "a yellow glass stops only 333 rays of heat, but stops 819 of light: on the contrary, a pale blue stops 812 rays of heat, and but 684 of light. Again, a dark-blue glass stops only 362 rays of heat, but intercepts 801 of light; and a dark-red glass stops no more than 606 rays of heat, and yet inter-

cepts nearly all the light, scarcely one ray out of 5000 being able to make its way through it *."

These experiments being made on undecomposed light, and on the radiant solar heat, either associated with it, or in one series separated by the prism, and also on the radiant caloric from heated bodies, a comparison can be less easily instituted from them, between the effect of transmission on the heating and illuminating powers of any single prismatic ray; and it may even be said, that they prove only the difference, in transmission, between the calorific rays and the luminous rays in general; not that the heating power of the coloured rays is owing to the presence of rays of caloric; for it does not necessarily follow, either that light of the refrangibility of any particular prismatic ray, must be stopped by a medium in precisely the same proportion as an undecomposed ray of light, or that the radiant caloric of the refrangibility also of that ray, shall be stopped in the same proportion as radiant caloric of a different refrangibility. It might even be granted, that the radiant caloric of heated bodies, or the radiant caloric which, when a solar beam is decomposed by the prism, is thrown beyond the red ray, is stopped by a medium in a very different proportion from visible light, without the inference being just, that such a difference must exist between the visible light of a single prismatic ray, and the radiant caloric supposed to be

* Philosophical Transactions for 1800.

associated with that ray. Dr Herschel has shewn, however, that by making every allowance for the differences in transmission from these causes,—differences which may be determined by experiment,—the conclusion still follows, that the heating and illuminating powers depend altogether on different rays, and that contradictions attend all endeavours to account for the results, by admitting the existence of visible heat,—in other words, of light possessed of a heating power.

It is unquestionably, however more directly conclusive, to have the experiment confined to a single prismatic ray; to separate it from the others, transmit it through a certain medium, and observe the effect produced on its illuminating and heating powers. If the ray be homogeneous, there will be a diminution in them in the same proportion, greater or less according to the degree of stoppage; while, if it be heterogeneous, or consist of rays of visible light and of radiant caloric, these will probably be unequally stopped, and the heating and illuminating powers must therefore be unequally diminished.

To take one ray as an example, and reduce the question to a single point: "Is the heat which has the refrangibility of the red rays occasioned by the light of these rays? Should that be the case, as there will then be only one set of rays, one fate only can attend them, in being either transmitted or stopped, according to the power of the glass applied to them." With regard to the fact in this point, Dr Herschel states, that from a series of experiments, he finds, that red glass does not stop red rays of light; "but with regard to

the rays of heat, the case is just the reverse; the red glass stops not less than 692 out of a thousand, of such rays as are of the refrangibility of red light." He adds, "Here, then, we have a direct and simple proof, in the case of the red glass, that the rays of light are transmitted, while those of heat are stopped, and that thus they have nothing in common but a certain equal degree of refrangibility, which, by the power of the glass, must occasion them to be thrown together into the place which is pointed out to us by the visibility of the rays of light *."

This conclusion seems irresistible. Did the heating power apparent in the red ray, (and of the different prismatic rays, it is the one which possesses it in the greatest degree), depend on the visible light of that ray, and belong to it as one of its properties; since this light is not stopped by red glasses, the heat likewise ought not to be stopped. Nearly two-thirds of the heat, however, are arrested, a decisive proof that that heat arises, not from the visible light of the ray, but from calorific rays associated with it, which, by such a glass, are transmitted only in this proportion.

The experiment, too, which has been so long known, of separating the light and caloric emitted from burning fuel, is a clear proof that the heating power does not depend on visible light. By placing a piece of transparent glass before the fuel, the radiant caloric is arrested, the light is transmitted, and may be collected in a focus, in which is no sensible heat. The absence of all heat in the rays of the moon con-

* Philosophical Transactions for 1800.

centrated in a focus, while the illumination is bright, affords a similar proof.

Some other circumstances are pointed out by Herschel, which lead to the same conclusion. Thus, in the experiment on the stoppage of solar heat and light by transmission through different substances, it is found, that the stoppage of heat is greater in the first, second or third minute, than in the fourth or fifth, while this does not happen in the transmission of light,—a proof that they obey different laws. It is also observed, that the effect of rough surfaces in scattering each kind of rays is different, being much greater on the rays of light than on those of heat. Similar facts are also found to hold true with regard to the illuminating and calorific rays emitted from burning bodies.

These discoveries, therefore, open to us entirely a a new view of the nature of light, and of the constitution of the solar ray. No fact appeared more undoubted than that light has a power of exciting heat, and when the solar beam was resolved into its different coloured rays, it was supposed that it was fully analysed, and that these were its sole constituent parts. We have now learned that both these propositions are false. A solar ray consists of the different visible rays of light; but with these are associated rays of caloric. These two *kinds* of rays not only differ from each other in refrangibility, but each appears to be composed of rays of unequal refrangibility. Hence, when decomposed by the prism, each is spread over a considerable space. The radiant caloric is rather less refrangible than the rays of light; it is therefore found beyond the visible prismatic spectrum on the

side where the less refrangible visible rays are; but being composed of rays of unequal refrangibility, it is not confined to that space, but is intermingled with the different coloured rays, diminishing as these become more refrangible. To this intermixture the heating power which these coloured rays appear to have in different degrees is to be ascribed; and apart from this radiant caloric we have no reason to believe that light has any heating power.

The last part of the history of Light is that which relates to what may be more peculiarly termed its Chemical Power,—its agency in occasioning decomposition, owing apparently to the affinities it exerts.

This power is in many cases strikingly exemplified. Next to oxygen, indeed, light is perhaps the most extensive in its influence of any chemical agent. These two principles may even be regarded as antagonists, the combinations of oxygen being generally attended either by the separation of light in a sensible form, or its transition into a state of new combination, while oxygen is scarcely ever disengaged without the interference of free or combined light.

Where this principle, oxygen, is not retained in combination by a very strong affinity, light alone is able to effect its separation, either partially or entirely. In the nitric acid, oxygen is in this state, and accordingly, by exposing this acid, which is colourless, to the rays of the sun, it soon acquires a yellow, and at length an orange hue,—a change which we know by other experiments is owing to a partial separation of its oxygen. If therefore the phial be filled with

the acid, and closed with a glass-stopper, the change, as Mr Kirwan has remarked, does not happen, the separation of the oxygen gas being prevented by this mechanical force; while, if the phial be only half filled, it takes place on exposure to the solar light for a quarter of an hour *. The experiment may even be conducted so as to obtain the oxygen which is disengaged from the acid. This was done long ago by Berthollet. The phial containing the acid having a bent tube connected with it, which terminated under an inverted jar; in a few days a considerable portion of oxygen gas was found to be disengaged, while the acid assumed more and more of the yellow colour †.

Another acid, the oxy-muriatic, suffers a similar decomposition from light still more easily. Berthollet exposed it in a flask, with a bent tube connected with the pneumato-chemical apparatus, to the light of the sun; in a very short time small bubbles of air were disengaged, which were collected, and found to be pure oxygen gas. The oxy-muriatic acid is of a yellow colour, but in proportion as this decomposition went on it became colourless; it was thus converted into simple muriatic acid, and from this very experiment Berthollet determined the proportions in which this acid combines with oxygen to form the oxy-muriatic ‡.

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* Notes to Scheele's Essay on Air and Fire, p. 230.

† *Journal de Physique*, t. xxix. p. 82. ‡ *Ibid.* p. 81.

A number of the compounds of metals with oxygen also suffer decomposition from the agency of light. If the oxides (as such compounds are named) of gold or silver be exposed to the solar rays, their colour becomes darker; and it is apparently from this cause that light always alters the shades of metallic paints. If the combinations of these oxides with acids be submitted to the same exposure, their colour is even more darkened. A piece of paper moistened with a solution of silver in nitric acid, is blackened in a few minutes: the muriate of silver, the *luna cornea* of the older chemists, is still more susceptible of this change, and is unquestionably the most delicate test of the chemical agency of light. Even in the twilight, it is remarked by Mr Davy, it slowly changes from white to faint violet, while the nitrate of silver is not changed *.

The decomposition of these compounds is even sometimes complete, and the metal is obtained in its original state. Scheele evaporated a solution of gold to dryness, and dissolved the dry mass in distilled water, poured it into a crystal phial shut with a glass-stopper, and exposed it to the beams of the sun. A fortnight after, a quantity of minute spangles of gold appeared in the solution, and the surface was likewise covered with a very fine pellicle of gold †. Mrs Fulhame, in the course of her experiments on metallic reduction, established the same facts. A piece of silk which was dipt in a solution of muriate of gold in wa-

* Journals of the Royal Institution, p. 173.

† Essay on Air and Fire, p. 83.

ter was exposed to the sun beams, and kept moderately wet with water during the experiment; the silk, from being yellow, acquired first a green, then a purple colour; at length particles of gold appeared on its surface, and, "in about an hour, the whole of the silk was covered with a superb coat of reduced gold." A piece of silk dipt in the same solution, and suspended over water in a phial covered with black silk, and put aside in a dark place, suffered no change in three months, except that its colour became slightly brown *. Mrs Fulhame found that a solution of nitrate of silver could be reduced in the same way by the action of light, while in the dark it suffered no change †.

It appears that in some of these cases the acid only of the compound is separated, which, however equally, proves the chemical agency of light. It had generally been supposed that the blackening of the muriate of silver was owing to the disengagement of at least part of its oxygen, and the approach of the silver to the metallic state; but Berthollet has shewn by experiment, that it is owing merely to the separation of a portion of its acid, which, when the experiment is made under water, is found combined in that fluid ‡. It has been proposed by Mr T. Wedgwood, by means of the changes of colour which these solutions suffer from light, to copy paintings on glass; a piece of paper, for example, moistened with a solution of nitrate of silver, being placed

* Essay on Combustions, p. 142. 146.

† P. 148. 151.

‡ Chemical Statics, vol. i. p. 147.

behind a painting on glass, and exposed to the solar light, the rays transmitted through the differently painted surfaces will produce distinct tints of brown or black, differing in intensity according to the shades of the picture, and where the light is unaltered the colour becomes deepest. The attempt has not succeeded, as no method has been discovered of preventing the unshaded parts of the delineation from being coloured by exposure to the light *.

The operation of bleaching affords another example of the changes which light is capable of producing. Colour is in this case indeed removed, but this depends equally on the transfer of oxygen, the colouring matter of the thread receiving that principle probably from the decomposition of the water with which the substance to be bleached must be supplied. Its colour is thus discharged, and it is also rendered capable of being extracted by the alkaline substances by which the operation is completed. This formed the old method of bleaching, and the substitution of the oxymuriatic acid under various forms in the new mode, affords a happy illustration of the theory of the changes of which the operation consists.

Even the processes of animated nature are influenced by the chemical agency of light. "Organization, sensation, spontaneous motion, and all the operations of life," says Lavoisier, "exist only at the surface of the earth, and in places exposed to the influence of light; and without it nature itself would be inanimate." In

* Journals of the Royal Institution, vol. i. p. 170.

vegetation it acts an important part, and its effects are strikingly exemplified in the adaptation of plants to particular climates. Those which grow under a clear sky, and an intense solar light, are in general more pungent, odorous, and aromatic, than those which are placed under the opposite circumstances; and plants which are the natives of a warm climate will not grow or produce their fruit in situations where they are less exposed to its genial influence. The artificial exclusion of light from vegetables giving rise to the process named Etiolation or Blanching, affords us the best view of its action in vegetation. The plant in such a situation always extends its branches towards any opening by which the light may enter; and if this be closed, and another opened in a different situation, it changes the direction in which it was shooting, and turns still towards the light; and in this way, as L'Abbe Tessier has shewn, plants may be made to grow in any direction. If kept in perfect darkness, they begin to suffer a remarkable change; become feeble, irritable, insipid, and of a white or yellowish colour, while, if transferred to a situation where they enjoy the solar rays, they regain their green colour, and become vigorous. It appears that these changes from the exclusion of light are owing to the accumulation of oxygen in the plant, and that under its influence this principle is disengaged from their leaves, derived probably from the decomposition of water, and perhaps of other compounds subservient to vegetable nutrition. According to the experiments of the Abbe Tessier, confirmed since by those of Decandolle, the light emitted by a lamp gives

even a green colour to the leaves, though much less deep than that from the light of day. The light of the moon has a similar effect *.

Nor are animals exempt from the influence of this important agent. Deprived of it they suffer nearly the same changes as vegetables do, and the darkness of their colour is in general greater according to the intensity of the light to which they are habitually exposed. Insects which live under ground are usually of a light shade: the animals of the arctic regions are almost all pale or white, while those belonging to the tropical countries are distinguished by the variety and brilliancy of their hues. Even in man we trace a gradation of colour proportioned nearly to the climate in which he resides.

It appears from the experiments of Chaptal that the process of crystallization, especially that form of it termed Saline Vegetation, in which capillary crystals shoot up the sides of a vessel containing a saline solution, is considerably influenced by light. According to his observations, it takes place most readily on the sides of the vessel which are opposite to the light; and on making a great number of experiments, he found that it took place only on the sides of the vessel which were illuminated; he could thus, at pleasure, cause it to rise at any side, and when the vessels were shaded, the line of separation between the part exposed to the light, and the part excluded was distinctly, marked by the limit of the

* *Mémoires de l'Acad. des Sciences*, 1783, p. 155.

crystallization. Metallic salts in general shewed this phenomenon best *.

Scheele proved, that the changes which have now been described, arise from the peculiar chemical agency of light, and not from its heating power. Some of them indeed, those for example which are experienced by the nitric and oxymuriatic acid, cannot be produced by heat; but Scheele further established, by a very striking experiment, the difference in the action of light and caloric. On exposing the substances, which he found to suffer changes from light, to the rays of the sun, in a phial covered with a thick coating of black paint, though the phial becomes very hot, the substances contained in it did not undergo the least change, even after an exposure for several days to the operation of the sun beams †. Berthollet made a similar experiment; that of exposing oxymuriatic acid to the rays of the sun, in a phial covered with black paper, when it suffered no alteration, nor gave out any air, as it does from the direct exposure to light. Did the light operate in these cases by the heat it excites, it is obvious, that under such circumstances the effects ought to be the same, or even greater, as even more heat would be communicated to the contained substances.

Rumford has stated some experiments ‡ to prove, that light has no peculiar chemical powers, further than what depend on the heat it excites, and that,

* *Journal de Physique*, t. xxxiii. p. 297.

† Essay on Air and Fire, p. 96.

‡ Philosophical Papers, p. 341.

therefore, heat will produce the same effects. Independent however of the discordance of such a conclusion with the preceding facts, the experiments of Rumford are quite inconclusive. He wetted a piece of ribband with a solution of muriate of gold, and held it stretched horizontally over the clear flame of a wax candle, at the distance of about $1\frac{1}{2}$ inch above the point of the flame. Though the gold was not reduced, the ribband assumed a purple colour, similar to that which it suffers from exposure to light. Wetted with nitrate of silver, the ribband exposed in the same manner, assumed a dark orange tint. When the ribband was placed by the side of the candle, at the same distance, it suffered no change. These partial reductions, he infers, are owing to the operation of heat, but from the nature of the experiment, no such inference can be drawn, since the influence of another cause much more powerful, which Rumford did not attend to, is present,—the ascent of inflammable matter with the current of air from the flame of the candle. We know, that in the clearest flame of this kind, the whole of the inflammable matter in the wick is not burnt, but is partly volatilized, and may be collected in fine powder, of the nature of charcoal, by holding a body with a clean polished surface, over the flame. Now we know, from the experiments of Mrs Fulhame, repeated by Count Rumford himself, that charcoal applied to these very solutions, effects their reduction; and we cannot doubt, therefore, of its agency in these experiments.

In another experiment which he made to support the same theory, he exposed pieces of charcoal, in a thin

glass tube, with a dilute solution of gold, to the rays of the sun: in less than half an hour, specks of revived gold appeared, and, at the end of the experiment, the surface of the charcoal in many places, and the inside of the glass tube, where it was in contact with the upper surface of the liquid, was covered with particles of gold. A tube was again filled with the solution and charcoal, but instead of exposing it to the rays of the sun, it was shut up in a tin case, and exposed in the dark, for two hours, to a temperature of 212°. The gold was in this case also reduced, and adhered to the surface of the charcoal. With a solution of silver, the effects were the same. From these experiments, however, no argument can be drawn; the introduction either of heat or light, was in some measure superfluous, since we find, from the experiments of Mrs Fulhame, that charcoal alone produces the effect*; and Berthollet, in repeating them, found, that in both cases, that is, in the exposure to light as well as to heat, the aërial products disengaged, shewed that it was the charcoal which had operated †. The heat may favour the action of the charcoal, as it does that of every decomposition, and the light may likewise, by co-operating with the affinity exerted by the charcoal, accelerate the effect, but this is no proof whatever of the identity of action. The question is, can heat *alone*, to the extent in which it is produced by the solar rays, produce the chemical effects which these rays *alone* occasion? We

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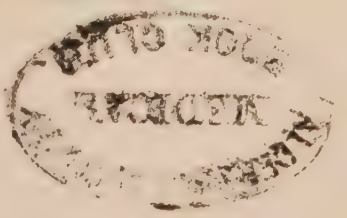
* Essay on Combustion, p. 124.

† Statics, vol. i. p. 149.



have no fact which proves this or renders it probable; in all those cases of changes from the action of light, which can be submitted to accurate experiment, the reverse is established; and it follows from them, that light is possessed of peculiar chemical powers.

What is the power of the different prismatic rays in producing these chemical effects? We are indebted to Scheele for the first observation on this interesting question. Having refracted the sun-beam by a prism, a piece of paper impregnated with muriate of silver, was put in the coloured light, and it became sooner black in the violet than in any of the other rays *. This experiment was repeated by Sennebier, who ascertained the comparative powers of the different rays. The shade produced in the muriate of silver, by exposure to the violet ray for 15 seconds, required for its production, the action of the purple ray to be continued 23 seconds, of the blue 29, of the green 37, of the yellow $5\frac{1}{2}$ minutes, of the orange 12 minutes, and of the red not less than 20 minutes †. In the experiments of Sir H. C. Englefield, it was tried, at the suggestion of Mr Davy, whether phosphorescence was unequally excited by these rays, and it clearly appeared, that the blue ray had a much higher power in rendering Canton's phosphorus luminous than the others.

The discovery by Herschel of the invisible calorific rays in the solar beam, and the analogy, that as there was a decrease in the heating power from the red ray,

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* Essay on Air and Fire, p. 91.

† *Mémoir. Physico-Chymiq.* t. iii. p. 199.

on one side of the spectrum through the others, so there was a decrease in the chemical power, in the contrary direction, from the violet towards the red, naturally suggested the inquiry, whether invisible rays distinguished by their chemical powers, might not exist beyond the violet ray.

Ritter, influenced by these considerations, appears to have made the first experiments on this subject. He placed muriate of silver without the solar spectrum, next to the violet ray, and found it to be blackened. On placing it beyond the red ray it not only did not suffer this change, but if previously a little blackened, became white; phosphorus was kindled in the one space, that beyond the red ray, and extinguished in the other. Exposed to the action of the violet ray, the muriate of silver was rather less blackened than in the space beyond it, where the invisible chemical rays existed, and still less in the others. He concludes, therefore, that there are two species of invisible rays, besides the visible rays in the solar beam, one species calorific, and which promote oxidation, the other deoxidating, or capable of separating oxygen when it is combined, and of counteracting its combination *.

Dr Wollaston had nearly about the same time made similar experiments, and, by the blackening of muriate of silver, had discovered the existence of invisible rays beyond the violet ray, capable of producing this chemical effect. He did not succeed in restoring the white colour to muriate of silver, after it had

* Nicholson's Journal, vol. v. p. 255. & vol. viii. p. 214.

been once tinged, however slightly, by exposure to the more refrangible rays. What is singular, guiacum, which is rendered green by exposure to light, apparently from the absorption of oxygen, suffers, according to Dr Wollaston, this change in the red rays of the spectrum, and at the other extremity it not only does not suffer it, but has its yellow colour restored *.

If we might reason by analogy, from the law proved by Dr Herschel to be observed in the refrangibility of the invisible calorific rays, to what may be observed by the invisible chemical rays, we should conclude that they may be of unequal refrangibilities,—that therefore they may not only exist in the space beyond the violet ray, but be spread over the prismatic spectrum, and that the visible rays may owe to them their chemical powers. We shall thus have three species of radiant matter in the solar beam, each distinguished by a single property not possessed by either of the others; the rays of light possessing the power of exciting illumination, or the sensation of vision; the rays of caloric producing heat; and the invisible rays, which are distinguished by their power of occasioning certain chemical changes. It has been affirmed, that Ritter, by transmitting the coloured rays through different prisms, has separated them from the chemical rays, and produced a coloured spectrum devoid of chemical action †.

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* Nicholson's Journal, vol. viii. p. 293.

† Ibid. p. 216.

From observing the intimate connection between light and caloric, some philosophers have been disposed to regard them as ultimately the same, or convertible into each other; while others, with perhaps more reason, regard them as totally distinct. This question is still the subject of discussion. Not being essentially connected with the chemical history of light, I have referred the consideration of it to the end of the volume. Note C.

CHAP. III.

OF ELECTRICITY AND GALVANISM.

FROM the phenomena denominated Electrical, the existence of a certain agent or subtle principle has been inferred. This principle, Electricity, besides the specific phenomena arising from its action, is productive of certain chemical effects, and is so far therefore an object of chemical science. There is reason to believe that Galvanism is ultimately the same principle with that on which electrical phenomena depend; there exist at least between them a very intimate connection; but as the modes of exciting them, and the effects they produce, are very dissimilar, I have placed their history under different sections.

Sect. I. *Of Electricity.*

If a glass rod be rubbed with the dry hand, or with a piece of silk, in a short time sparks or flashes of light will dart from its surface; and on approaching to it small pieces of straw, or other bodies easily moved, these will first be attracted towards it, and in a short time will be again repelled. All bodies, however, are not susceptible of being brought into this state, or, when subjected to the same or greater friction, do not present the same phenomena. If the above experiment be repeated with a metallic rod, not only have we not the same appearances, but no sensible effect is produced. Hence the distinction of bodies in their relation to electricity into two classes; Electrics, or those which afford it, from friction, and Non-electrics, or those which are incapable of being excited, or of presenting, from that cause, electrical phenomena.

If, when an electric is under excitation, a non-electric be brought nearly or altogether into contact with it, the electricity which is accumulated in the former is immediately carried off by the latter. But if an electric be applied in the same manner to the one which has been excited, it will not withdraw, or carry off the accumulated power. Hence another distinction is established, of Conductors and Non-conductors; the latter being the same as electrics, or those in which electricity is excited by friction, the former the same as non-electrics, which are incapable of this excita-

tion. Glass, resinous substances, sulphur, oils, and aëriform fluids, are the principal non-conductors; the principal conductors or non-electrics, are metals, a number of saline and earthy substances, and water. But, by certain arrangements, some belonging to the one class may be made to receive the property which is characteristic of the other.

If the electric, which is subjected to friction, be insulated, that is, supported on another electric or non-conductor, the quantity of electricity evolved is inconsiderable, and is soon limited. But, if a communication of it with the earth be established by the medium of a conductor, it will afford electricity as long as the friction is kept up; and a conductor insulated, if placed before it, will receive the electrical power, and retain it until another conductor is applied to it, when the accumulated electricity in the former will be instantly carried off. In this way a stream of electricity can be obtained; or it may also be procured in a more concentrated state; and on these principles, the common electrical machine, by which these effects are obtained, is constructed,—a glass plate or cylinder being made to revolve against a cushion, which is supported on a glass pillar, but connected with the earth by a metallic chain, and a large metallic tube, the prime conductor, being placed before the plate or cylinder, and insulated by being supported on a pillar of glass. The electricity excited by the friction of the plate or cylinder against the cushion, is collected by the prime conductor, and on the approach of any conducting substance, instantly passes off under the form of a stream or spark.

Electricity, then, is excited by the friction of an electric; but different electric substances, or the same electric under different circumstances, will exhibit different phenomena under a state of excitation. If a glass rod be excited by friction with a piece of woollen cloth, on approaching to it a light body, as a small bit of cork, the cork is first attracted; in a short time it is repelled, and is not again attracted until it has been touched by a conducting body. But, if a rod of sulphur has been excited by friction with the cloth, the cork, in the state in which it is repelled by the glass, is attracted by the sulphur, and on the other hand is repelled by the sulphur, when in that state in which it is attracted by the glass. These electrics present also the electrical light under different forms. If a pointed conductor, as a needle, be presented to the glass, a round lucid point appears on its extremity in the dark, but if presented to the sulphur, a pencil of rays seems to issue from the needle. And if two bodies in these different states be brought into contact, or be made to communicate by a conductor, the electricity in the one appears to destroy that in the other, and the electrical phenomena cease. These two electricities being first obtained, the one from glass, the other from sealing wax and other resinous bodies, by friction, were at first termed the Vitreous and the Resinous, and were regarded as essentially different.

It was discovered, however, that when two electrics are rubbed against each other, the one acquires always the one electricity, the other the other. Thus, in the

common electrical machine, when the cushion is insulated, on friction being made it exhibits what has been termed the resinous, while the glass gives the vitreous electricity. And, by certain management, particularly employing different substances to excite friction, or by altering the surface, the same electric may be made to exhibit either electricity, glass the resinous, and sulphur or sealing-wax the vitreous.

Franklin, from such facts, was led to deny that these electricities were different, and to explain the phenomena on a more simple hypothesis,—that there exists only one agent, by which they are produced, —a fluid highly elastic, or repulsive of its own particles, but attracting and attracted by the particles of other matter;—that in all bodies a portion of this subtle principle is present, and when present in them, in the proportion natural to each, they exhibit no electrical phenomena; but, if subjected to certain operations, particularly to friction, the equilibrium is disturbed, and the body either acquires more, or has less, than its natural proportion. In the former case it is said to be electrified *plus*, in which state it presents the phenomena ascribed to what was called the vitreous electricity: in the latter case it is said to be electrified *minus*, which corresponds with the state of resinous electricity; and instead of these terms, the phrases Positive and Negative electricity are employed in the Franklinian theory. This theory, or rather hypothesis, accorded with the phenomena of electricity, and in particular gave a happy explanation of the discharge of the Leyden phial. Hence electri-

cians have in general been disposed to prefer it. It has never been established, however, by any very rigorous evidence, nor has the opposite hypothesis been disproved, or even shewn to be inconsistent with facts. Assuming the existence of two fluids, each of which repels its own particles, but attracts those of the other, which are contained in all bodies, but are separated by certain causes, particularly by friction, which when separate give rise, and that in proportion to their quantity, to what are termed the Positive and Negative electric states, and which when united produce that equilibrium which is not discoverable by any electrical phenomena,—admitting these assumptions, the phenomena of electricity can be explained. The experiments, which have been supposed to show the direction of the motion of the electric fluid, and by which of course the positive and negative states of a body with regard to it, it is imagined are discovered, are admitted to be fallacious or inconclusive, and are solved on the hypothesis of two fluids, by the supposition that the facility with which the one is conducted, or the resistance opposed to it by the varieties of matter, is somewhat different from that opposed to the other. The only advantage which the system of Franklin can claim, is its superior simplicity. On the other hand, from the phenomena of galvanism it appears that the two electricities, whatever may be their nature, exert different chemical agencies; a fact not very favourable to the supposition that they are identical, and differ only in the condition in which they exist. Whatever theory be

adopted, it has from this fact become necessary, in their chemical history, at least to distinguish between them.

The chemical agency of electricity may be in a great measure ascribed to its power of exciting a high temperature. The mode in which it does this, or the nature of its relation to caloric, is, however, rather obscure. It appears, that in passing through any body in such a quantity that it is not accumulated, or does not meet with resistance, it does not produce any sensible heat. Van Marum placed the bulb of a very sensible thermometer in a cavity in a brass plate, five inches in diameter, and eleven in length, which was suspended by silk strings near the conductor of his powerful electrical machine. Neither from positive nor negative electricity was there any rise of temperature, nor was any perceived when the bulb was placed in a cavity in a piece of charcoal. But if the bulb of the thermometer were suspended loose between two conductors so as to have the stream of electric matter directed upon it, it rose with a powerful apparatus 80 or 100 degrees of Fahrenheit's scale, and this whether the experiment were made *in vacuo*, in atmospheric air, or in any other gas *. When a thermometer is placed between imperfect conductors, its temperature is raised. Nairne observed, that when the bulb was placed in the luminous current between two balls of

* Philosophical Magazine, vol. viii. p. 193.

of wood, it rises 32 degrees; and Van Marum found, that in placing it in a cavity in a rod of wood, placed between the ball of the conductor and the conducting wire of his apparatus, it rose in five minutes from 61° to 112°. In its concentrated state, under the form of the spark, it is even capable of kindling inflammable bodies, as ether, or spirit of wine; or if transmitted through mixed gases, the particles of which have mutual affinities, it acts on the mixture as a spark from an ignited body would, and by its heating power causes them to combine. This power is of course still more conspicuous in the discharge from a coated jar, or from an electrical battery; a heat is produced, not only sufficient to cause inflammables to burn, but, according to the strength and celerity of the discharge, to ignite, and even to melt the most refractory of the metals, and form them into globules. From the highest charge of a battery, containing 135 square feet of coated surface, Van Marum found he could fuse 180 inches of iron wire, $\frac{1}{150}$th of an inch in diameter, or 6 inches of iron wire $\frac{1}{40}$th of an inch; from a charge of a battery of 350 square feet of coated surface, 25 inches of the latter wire were melted; and, according to a subsequent experiment from the discharge of a battery of 550 square feet of coating, an iron wire, $\frac{1}{40}$th inch in diameter, and 24 inches long, was thrown to a distance in small red-hot globules. A discharge on quartz, one of the most infusible minerals, rounded its corners and points, and even fused a part of it.

The power of the electric fluid in thus exciting a

high temperature, appears, therefore, to be proportioned to the resistance opposed to it in its transmission: hence a small quantity of it passing through a perfect conductor produces no heat; and when heat is excited, it is regulated in a great measure by the quantity transmitted, and the volume of the body through which it is made to pass. The same quantity which, if passed through a metallic wire of moderate thickness, will produce little or no heat, on being transmitted through a similar wire, but of only one-tenth the diameter of the other, will extricate a quantity of caloric sufficient to melt it.

Though this be true, however, to a certain extent, it is not strictly so. In other words, if a wire of a given diameter be melted by the discharge from a given coated surface, a wire of double the diameter will not be melted by the discharge from double that surface, but on the contrary will require a much larger quantity. And a very singular fact is to be remarked on this subject, that if a quantity of electricity be discharged on a metallic wire, sufficient to melt it, on discharging on the same wire a quantity a little less, we do not obtain a rise of temperature a little inferior to what was excited in the first experiment, but a rise which is comparatively extremely inconsiderable. A wire of platina was melted by a shock of a certain strength; discharges a little weaker were transmitted through a similar wire, and the temperature they excited, instead of approaching to the intense heat necessary to fuse platina, was estimated not to exceed

that of boiling water *. From this fact, Berthollet revives an opinion which was once maintained by electricians, of what was termed a Cold Fusion being produced by electricity; or as he states it, the electricity operates in fusing bodies, not "by an elevation of temperature, but by a dilatation which separates the particles of bodies." The hypothesis is not a very clear one; and in reference to this very question, it has been proved, that when a body loses its solidity from an electric discharge, it is actually fused, and with an increase of temperature †, however the fact may be explained, that a charge somewhat inferior to this does not raise the temperature near to the fusing point.

Van Marum found, that the fusibilities of the different metals by the electric fluid are different from their fusibilities by the direct application of caloric. The same quantity of electricity was discharged through wires of the same diameter of the different metals. 120 inches of zinc were melted; the same of lead; of iron 5 inches; of gold $3\frac{1}{2}$; and of silver and copper not quite a quarter of an inch. Hence, it appears, that lead and zinc are equally fusible by the electric fluid, though to melt them by the direct application of caloric different degrees of temperature are requisite; and iron, though much less fusible than gold or silver by heat, is melted in greater quantity by the

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* Chemical Statics, vol. i. p. 423.

† Priestley's History of Electricity, 4to, p. 317–18.

electric fluid. It is possible that different metals may differ somewhat in the resistance they oppose to the transmission of electricity, and perhaps also the heat excited by that agent may be similar to that produced by friction or percussion, of course connected with the vibratory motion of the bodies subjected to it, and therefore in some measure dependent on the capability of bodies of being put into such a state.

From its power of exciting heat, electricity often favours chemical combination, and in particular cases is a more convenient form of applying heat for that purpose than any other. Its power in promoting combination is well exemplified in the change it produces on the surface of metals through which it is transmitted, while they are exposed to the atmospheric air. It causes them to combine with the oxygen of the air, or their surface suffers precisely the same change as when under the same exposure they are exposed to heat; and if the electric discharge has been powerful, the change is effected through the whole substance of the metal. In this way, all the metals may be oxidated, even those which resist the application of common fire, as has been shewn by Mr Cuthbertson in a series of experiments on this subject *. It is principally, however, to promote the combination of gaseous bodies that electricity is applied. The apparatus employed is a thick glass tube, Pl. VIII. Fig. 58., her-

* Nicholson's Journal, 4to. vol. v. p. 147.

metically sealed at one end, the sides of which, at about the distance of two inches from the sealed end, are perforated with small holes, in which are fixed by cement two metallic wires, the extremities of which, within the tube, are distant one-fourth of an inch. This instrument being filled with water or quicksilver, and inverted, a quantity of the gases intended to be combined, mixed in the due proportion, is introduced, so as to depress the fluid an inch or more beneath the wires. The electric spark is made to pass from the one wire to the other, by connecting one of them with the conductor of the common electrical machine, and hanging a chain on the other. Sometimes only one wire is inserted in a perforation in the head of the tube, and fixed with cement, represented Fig. 59.; it is of such a length as to descend three or four inches within it; and when connected with the electrical machine, the spark issues from its extremity within by the conducting power of the fluid beneath, which must of course be distant from it not more than half an inch. In the mixture of some gases a single spark be sufficient to cause the combination to proceed through the whole mixture, so much caloric being evolved from the action of the particles first combined as to cause the instantaneous combination of the others. In other cases, a stream of sparks requires to be transmitted to produce the combination to any perceptible extent.

By the same agency, electricity is able to effect chemical decomposition. If the spark be taken in a compound gas, ammonia, or nitrous gas, for example, it se-

parates its constituent parts; if an interrupted electrical discharge be sent through water, it is attended with the disengagement of a small quantity of elastic fluid, and when repeated sufficiently to admit of this being examined, it is, as Dr Pearson has shewn, a mixture of the two gases which form water. Other compound fluids are decomposed in a similar manner, as liquid ammonia and alkohol; and if the metallic oxides be exposed to a very strong explosion from a battery, they are reduced to the metallic state *.

The electric fluid is also intimately connected with light, and to this some of its chemical effects are probably, in part at least, to be attributed. When it passes through the air from one conductor to another, it exhibits a luminous spark; when discharged through a vacuum the most perfect the air-pump can produce, it presents very vivid corruscations; these appear even, though more faintly, in the Torricellian vacuum. In transmission through any fluid, if the quantity of fluid be not large proportioned to the discharge, it is always rendered luminous †; or if discharged in large quantities over the surface of a solid, a brilliant illumination is produced. The electrical light is also heterogeneous, or consists of the different refrangible rays. Priestley observed these by a prism; and Morgan has remarked that the electric light may be made to assume different colours according to the medium in which it is taken; sometimes the more refrangible rays being separated,

* Philosophical Magazine, vol. viii. p. 197. 319.

* Philosophical Transactions, vol. lxxv. p. 198.

sometimes the less. A spark conveyed through a vacuum not perfect, displays the indigo rays; taken in the vapour of ether it is green, and in ammoniacal gas red. Or if the electric discharge be transmitted over a piece of insulated wood, by placing the wires between which the discharge takes place at different distances from the wood, the light will exhibit nearly all the prismatic colours *.

It may be doubted if electricity could produce some of the chemical changes it does, had it not this connection with light. In decomposing water, or reducing the metallic oxides, it is necessary that it should be capable of affording light to the principles it separates, as these contain light as a constituent part. A portion of water may be decomposed in a tube by the electric discharge, and by transmitting the spark through the gases into which it is resolved they combine, the combination being accompanied with a flash of light, and this may be repeated any number of times. The light thus contained in the gases, and extricated when they combine, must at their evolution from the water have been derived from the electric fluid.

The chemical agencies of electricity are as yet, however, but imperfectly developed, and there are a number of facts which prove it to be absorbed or evolved in chemical changes where its influence has scarcely been traced. The electrical phenomena exhibited by the tourmalin shew that electricity is excited, and its different states produced, in some cases merely by variations of temperature. Even its excitation in the electrical machine is promoted by chemical action, as

* Philosoph. Trans. vol. lxxv. p. 205.

on this appears, in a considerable measure, to depend the effect of the amalgam applied to the rubber, the power of which is greater when it is composed of oxidable metals than of those which are not so susceptible of oxidation, as has been clearly proved by the experiments of Wollaston *. The experiments of Wilcke and Æpinus shew that in fusion and congelation the different electricities are excited, and the states of *plus* and *minus* produced in the body which has suffered the change of form, and the matter with which it has been in contact during the change; this happens too in the formation and condensation of vapour, and Volta traced it in different cases of chemical action. The observation of such facts becomes more important since the connection of electricity with galvanic phenomena has been established, and that connection has itself more clearly demonstrated the importance of Electricity as a chemical power.

Sect. II. *Of Galvanism.*

Galvanism is supposed to be essentially the same principle as electricity. Of this, however, some doubts have been entertained, and whatever may be the decision on this question, its effects, its mode of production, and the laws which it observes in its action, are so far dissimilar, that it is proper to consider it under a separate section. Our knowledge of galvanic phenomena is of very recent date, and being yet so little advanced with what will probably be the result of farther investiga-

* Philosophical Transactions for 1801, p. 433.

tions, it will be sufficient to state those facts with regard to its production and agency, which are well ascertained, which lead to important consequences as to its chemical operation, or which serve to generalize its phenomena.

Galvani, an Italian physiologist, observed the first striking phenomenon which, becoming the subject of investigation, led to the discovery of the principle which has from him derived its name.

Some observations having occurred to him on the facility with which the muscular fibres of a frog are excited to contraction by electricity, he was induced to make some experiments from which the discovery resulted, that by merely applying a conductor of electricity to the nerve and muscle of an animal, contractions could be excited. This led him to conclude, that the two parts are in different states of electricity, one *plus*, the other *minus*; and that the application of the conductor causes the discharge, whence the contraction in the muscle. The subject was prosecuted by some other physiologists, and the term Animal Electricity was applied to the agent concerned in this phenomenon, from the hypothesis that it was generated in the animal system,—an hypothesis apparently justly deduced from these phenomena, and confirmed by the analogy drawn from the electrical animals, the Torpedo, Silurus electricus, and Gymnotus electricus, from whose singular economy sufficient proofs were obtained of the power of the living system to produce electricity.

Volta, to whom, more than to any philosopher, we are indebted for our knowledge of Galvanism, consider-

ed these phenomena under a different point of view. It had been found, that by coating the nerve of the animal with metal, the contractions excited were considerably stronger; and Volta concluded that the electricity is generated by the metal, not by the animal; and that the introduction of living matter into the arrangement, serves only to render evident the generation of small quantities of this power. His experiments shewed that the connection of a nerve with a muscle was not requisite, but that if two metals be applied to different parts of a single muscle, on connecting them by an electrical conductor, contractions are excited. He shewed also that in a similar way *sensations* could be excited, that when one metal, for example, is applied to the under surface of the tongue, and another to the upper surface, on bringing their edges into contact, or connecting them by a conductor, a peculiar taste is instantly felt *.

For some time the prosecution of these experiments, and the discussion of the questions, whether these phenomena arose from electricity, or from a principle analogous, but still different; and whether this principle was generated or not in the animal system, engaged the attention of philosophers. At length the capital discovery by Volta of a mode of augmenting greatly the galvanic energies, demonstrated the falsity of the hypothesis that its production is a process of vitality, extended these investigations, and in particular led to the discovery of the chemical agencies of this power.

Hitherto galvanism had been excited by the contact or communication of two plates only, of metals but

* Letter of Volta, Phil. Trans. 1793, p. 10.

it occurred to Volta, that by employing a number of plates, and establishing a connection among them, the effect might be much increased. This gave rise to the Voltaic pile, of which Volta transmitted an account to the Royal Society of London *. To construct it, a plate of metal, suppose of silver or copper, is placed on any support; on it is placed a similar plate of another metal, suppose zinc, and over this a piece of card or cloth of the same size, previously moistened; this series of silver, zinc, and moistened card, is repeated in the same order, and in this way a pile, consisting of 20, 30 or 50 pieces of each metal is reared, as represented, Fig. 61. Pl. VIII. In this arrangement we have the accumulated action of the pieces of which it consists, and accordingly the effect is proportionally great. If the finger, moistened, be applied to the top of the pile, and another finger, moistened, to the under plate of the pile, the moment this contact is established, a pungent sensation is felt, somewhat similar to an electrical shock.

Another arrangement, similar in principle, which Volta sometimes used, and which in particular is convenient in ascertaining the powers of different fluids, is that which he names the *Couronne de Tasses*, represented, Fig. 64. It consists of a series of glass cups nearly filled with water, a saline solution, or whatever fluid is used to promote the production of galvanism. In the first is put a plate of metal, suppose silver; from this plate there is a wire or thin flat piece of the same

* Philosophical Transactions for 1800, p. 403.

metal, which, by a curvature, can be inserted also into a second cup, in which is placed a plate of a different metal, suppose zinc, to which this wire is also attached. We have thus the two metals connected by a metallic arc, with fluid surrounding them. In the second cup is placed another plate of silver, at a distance from the zinc, which, as in the former, is connected with a plate of zinc in a third cup; and in this manner the series is carried on.

With the pile of Volta a number of experiments were soon made by the British chemists, and by them was discovered its agency in producing chemical effects. Mr Carlisle and Mr Nicholson found, that at the two extremities of the pile, electricity was in opposite states; in that which commences with the more oxidable metal, the zinc or copper, it is *plus*, in that terminating with the silver, it is *minus*, as Volta, by the aid of his condensor, had before observed. The electric spark was also perceived: and observing accidentally, that from a globule of water on the upper metallic piece of the pile, a small stream of gas arose, which had the smell of hydrogen, Mr Nicholson proposed to introduce wires, connected with the two extremities of the pile, into a tube filled with water. Immediately on making this experiment, a stream of hydrogen gas arose from the wire connected with the minus side of the pile, and the wire connected with the other appeared to be oxidated. On employing wires of a metal not easily oxidable, as platina, a stream of gass issued from each, that from the one being hydrogen, from the other oxygen *.

* Nicholson's Journal, 4to. vol. iv. p. 179.

These experiments immediately attracted attention, and were prosecuted by Messrs Cruickshank, Wollaston, Davy, Henry, Haldane, and other British chemists, by whom a number of interesting facts on the chemical agencies of this power were observed; and Mr Cruickshank, by his invention of the galvanic trough, so much more powerful and convenient than the pile, facilitated greatly these inquiries. The Continental philosophers, in a short time, also began the investigation of the subject. Fourcroy and Vauquelin, Thenard, Van Marum, Tromsdorff, Ritter, and Volta, have added a number of important facts. From the materials thus amassed, I shall present a statement of the effects and laws of galvanism.

The apparatus by which it is produced and applied, is first to be described. The Trough invented by Mr Cruickshank, is preferable to every other arrangement, and is at present always used. It consists, Fig. 65. of a hollow box or trough, of hard and well seasoned wood, in the sides of which are cut small groves, at the distance from each other, of from $\frac{1}{4}$ to $\frac{3}{4}$ of an inch, according to the width of the box. Plates of two metals, generally of copper and zinc, not less than 2 or 3 inches square, and often much larger, are soldered firmly together, and this soldered or double plate, is inserted in the groove of the box, and fixed in it by a cement of resin and wax, so well applied that no liquid can pass through. This is repeated, fixing a double plate in each groove, and taking care that the order in which they are inserted shall not be reversed, but that if the copper side of the double plate has been next to the ex-

tremity of the trough at which the insertion has commenced, the copper sides of all the others shall be in the same order, and the zinc side of the last plate shall therefore be opposite to the other extremity. The grooves thus filled by the metallic plates, being at a certain distance from each other, there are of course cells or cavities between them, and these are designed to contain the fluid by which the galvanism is excited, or they serve the same purpose as the moistened cards or pieces of cloth in the pile of Volta.

This arrangement is possessed of great advantages, compared with the pile. The surfaces of the two metals which are in contact, by being soldered, at least at the edges, are prevented from suffering any chemical change, by which their conducting power would be impaired, and the cells containing so much liquid, the trough can be preserved longer in action, than the pile, in which the moistened cards soon become dry; and the action from a given surface of metal, is also from the same cause more energetic. It is also much less troublesome to put the apparatus in a state of action, and keep it clean.

The metals used are generally zinc and copper, and these, on the whole, answer best; silver and zinc, from experiments with the pile, appear to furnish a more powerful combination, but the difference is not very considerable, and by no means such as to compensate for the difference of expence. The number of plates, and their surface, as I shall immediately have to state, must be regulated by the purpose to which the trough is to be applied. The wires for conducting and applying

the galvanism generated in the trough, should be of a metal not much liable to chemical change; those of gold or platina have this advantage.

Different fluids are employed to fill the cavities of the trough, and differ much in their power. With water, the effect is very inconsiderable; with a solution of sea-salt (muriate of soda) or of muriate of ammonia, the effect is much greater, it is still more so, though perhaps it ceases sooner, with diluted muriatic or nitric acid: the last, on the whole, is preferable to any other; one part of nitrous acid, of the usual strength, or about the specific gravity of 1.4 or 1.5, being diluted with 30 parts of water. By this fluid, too, the surfaces of the plates are kept always clean, as it dissolves the oxide formed. If muriatic acid, which is less expensive, be used, the proportion may be one part to 20 or 25 of water. A solution of sea-salt in water, to which a little muriatic acid is added, produces the effect very well; it is rather less powerful than the diluted nitric acid, but it continues to act longer. When the trough has been used with any of these fluids, it requires merely to be washed with water at the end of the experiment.

From the experiments of Van Marum, it appears, that insulating perfectly the voltaic apparatus, considerably adds to its power *.

Though the arrangement now described,—that of two metals, with certain chemical fluids, be the one

* *Annales de Chimie*, tom. xl. p. 305.

generally employed, it is not the sole one from which galvanism may be generated; and as illustrative of the theory of its production, several important facts require to be stated.

The combination of a single metal with a fluid excites galvanism, as can be discovered from the power of such a combination to excite contraction in the muscles of a prepared frog; but no accumulating series of this kind can be formed. A metal acted on by two different fluids, affords an arrangement, the powers of which is augmented by repetition, though in different degrees, according to the nature of the fluids. If a series be formed of water, metal, diluted nitric acid, the production of galvanism is evident, though not considerable. One somewhat similar in power, is formed from the series, water, metal, sulphuret of potassa; while from the series, dilute nitric acid, metal, sulphuret of potassa, the production is much greater than from the other, as Mr Davy has ascertained *. He observed, too, that a piece of charcoal, in contact at one of its surfaces with water, at another with nitric acid, shews signs of galvanism, and a galvanic arrangement may even be formed, without the intervention of metal, of different kinds of animal matter.

Volta has generalized these facts, and has given the following clear summary of productive galvanic arrangements. After dividing the conductors of it, or

* Philosophical Transactions for 1801.

of electricity, (as he considers them the same), into two classes, perfect and imperfect; the first, comprising the metals, some native metallic combinations, plumbago and charcoal; the latter, including chiefly water, saline solutions, and the animal fluids; he adds, "If in a series of three conductors, which touch two and two, we place either a conductor of the second class, between two different ones of the first, or one of the first class between two different ones of the second, or finally, if we form a circle of three different conductors of the second class, without the intervention of any of those of the first,—in these three cases, a current of electricity will be established passing to the one extremity or to the other, according to the predominating force of the substances arranged, which will cease only on breaking the circle, and will be re-established, when, after such an interruption, it is restored. Of the first arrangement, we have an example in two metals with a humid disc; of the second in a single metal, with diluted acid on the one side, and sulphuret of potassa on the other; and of the third, Volta gives the instance of muscle, nerve, and the blood of an animal recently dead *." In these arrangements, it is not indifferent what conductors of the same class are used; some, as has already been stated, being superior to others.

The properties of Galvanism are next to be stated.

It passes through those substances which are conductors of electricity, and, in general, with the same

* *Journal de l'Ecole Polytechnique*, tom. v. p. 286.

differences of ease and rapidity. Hence the metals are the best conductors of galvanism; the power of charcoal, in this respect, is somewhat equivocal, as it is also with regard to electricity; some pieces at least conducting imperfectly, while others are very perfect in conducting power. Plumbago is also a conductor. Different fluids,—water, saline solutions, and others, all conduct it, as is obvious from their forming part of the galvanic circle in the trough or pile. Glass is a non-conductor with regard to it, as are also dried wood; and what is singular, the dry animal cuticle, which is pervious to electricity. Gases not humid appear also not to conduct it.

In its transition from one conductor to another, especially where the conductor is an imperfect one, it produces intense light. If the wire issuing from one extremity of the trough be made to touch the wire that comes from the other, at the moment of contact, and every time it is renewed, a spark more or less vivid, according to the power of the trough, is excited. Its appearance is the same at whichever wire it appears. If the wire be made to touch a piece of plumbago, or well-burnt charcoal, which is connected with the opposite wire, the spark is more vivid; and if each of the wires be terminated with small pointed pieces of well-prepared charcoal, on bringing them into contact, the light excited is the most intense and pure which we can produce by any artificial arrangement; if the trough is a large one, innumerable rays dart from the point of contact, and continue to do so while the contact is preserved. This galvanic light

seems principally to arise from the accumulation of the fluid, and not from combustion; for it is attended with very little waste of the metal or charcoal, and it can also be easily excited, though not with equal splendour, under water, oil, alkohol, and other fluids, and in gases not capable of supporting combustion. In air, a slight degree of burning, however, does perhaps attend it, from the degree of heat which it excites; and hence the light is somewhat increased, by placing the charcoal in oxygen gas.

Galvanism may also be applied, however, so as to excite very intense combustion, and to cause even bodies to burn which do not suffer that change in any other way. This happens when it is applied by one metal to others drawn into fine wire, or beat into fine leaves. If leaves of gold, silver, copper, tin, and other metals, be suspended from a wire connected with one extremity of the trough, on applying to the edges of them a metallic plate, connected by a wire with the other extremity, the leaves immediately enter into a vivid deflagration, with the emission of different coloured lights, and the metals are found to have suffered that chemical change, which is perfectly analogous to combustion. A fine iron-wire connected with the one end of the trough, when run along a plate attached to the wire connected with the other, burns, with the emission of numerous small vivid sparks. The inflammable gases are made to burn by the galvanic spark when sufficiently strong, if they are in contact with the air; or, if mixed with oxygen, they explode on its introduction. The heat which galvanism excites, inde-

pendent of the combustion of the substance it is applied to, is shewn by placing a wire in water, forming part of the circuit, when the water is soon made to boil, as is also expressed oil. The metals also, iron or platina wire for example, can be ignited, and even fused, independent of their combustion, by the rapid transmission of the galvanic fluid. Their ignition, too, is produced, when they are placed in gases not capable of supporting combustion *.

The powers of galvanism in producing chemical decompositions are striking and peculiar. The general method of exemplifying them, is to bring two wires connected with the two extremities of the trough, one with each, within a short distance of each other, (about one-fourth or one-half inch), in a compound fluid, contained in a glass-tube. The decomposition almost instantly commences, and where the compounds which it decomposes, consist of gaseous principles, gas is evolved at each wire. Thus, in water, which is a compound of two gases, oxygen and hydrogen, each of these is extricated at the extremity of one of the wires; oxygen gas at that which is connected with the zinc or more oxidable metal; and hydrogen at that connected with the other,—a phenomenon which presents some difficulties, and according to late experiments also some singular facts, as to the production of certain other chemical agents, which will afterwards be the object of consideration. In alkohol, the decom-

* *Journal de l'Ecole Polytechnique*, t. iv. p. 292.

position is equally rapid, and the products are aërial, consisting of new combinations of its constituent principles; in oil there is a similar decomposition. Ammonia dissolved in water, exposed to its action, affords its elements, mixed with variable proportions of those of the water. The compound acids, too, are decomposed; nitric acid evolves its two gaseous principles; and from sulphuric acid sulphur is deposited, and gas evolved. It is not improbable, that some of these decompositions may be effected by the action of the nascent hydrogen from the decomposition of the water present. The influence of this is very well shewn in the formation of ammonia in the wire evolving hydrogen, when water not freed from air is submitted to the galvanic decomposition; and likewise by the revival of metals dissolved in acids, when such solutions are subjected to the action of the same wire; the reduced metal appearing in filaments at the extremity of the wire.

When the galvanic influence is made to operate in these decompositions, not by the medium of metallic wires, but of small pieces of charcoal, the results are nearly the same, the products only being modified by the combinations of part of the charcoal with the gases evolved.

These chemical actions take place even when the wires from the two extremities of the galvanic battery are placed in portions of the fluid, in separate vessels, provided these vessels are connected by water, or a perfect galvanic conductor; but if the communica-

tion be interrupted, the action going on at the extremity of each wire immediately ceases.

Though the effects of galvanism on the living system are not chemical, yet, as connected with its general agency, it may be briefly stated, that a sensation somewhat similar, though by no means precisely the same with that from the electrical discharge, being less concentrated and pungent, is felt when the two extremities of the galvanic battery, or conductors connected with them, are touched. It is experienced only at the moment of contact. If the battery is weak, it extends only up the fingers; if stronger, it is felt at the wrist, or even to the shoulder. Contractions of the muscles are at the same time excited.

I have now to state the law with regard to the production of these effects, by which their intensity is regulated.

It is sufficiently obvious, that by increasing the number of pieces which compose the galvanic arrangement, its powers are increased, since this is indeed the very principle on which its agency depends. If a pile or trough composed of 20 pair of plates, act with a certain degree of force, one of 30 or 40 will act with still more; and to obtain a great galvanic power, arrangements of 200 or 300 plates have been constructed.

Since galvanism is generated by the contact of metals with each other, or with the fluid applied, it may also be expected, that an enlargement of the surface will increase the effect; and this is accordingly found to be the case to a certain extent.

A singular fact, however, was discovered by Thenard, Fourcroy, and Vauquelin, that an increase in the mere number of plates, without a proportional increase in their surface, does not augment equally all the effects obtained from galvanism; but that a different law is followed in the increase of the power of igniting the metals, and in that of giving the shock to animals, or decomposing chemical compounds. They found that the power of igniting the metals, depended principally on surface; so that a few large plates, twelve of 12 or 20 inches diameter, caused them to burn with the greatest brilliancy; while the same plates, divided into 48, produced a very inconsiderable effect. On the other hand, the power of giving the shock, and of producing chemical decompositions, is rather dependent on number; the twelve large plates will give a very feeble sensation, or decompose water slowly; while, if cut down, so as to form an arrangement consisting of 40 or 50 small plates, their powers with regard to these effects will be greatly enlarged *.

Some explanation may be given of this striking difference: Fluids are much less perfect conductors of galvanism than the metals, hence from the extent of the series of imperfect conducting matter which it has to pass through in an arrangement composed of a great number of plates, its velocity is retarded, it is, as it were, accumulated, becomes more concentrated, or has its *intensity* increased. And as the shock is dependent principally on this intensity, as is proved by

* *Journal de l'Ecole Polytechnique*, tom. iv. p. 291.

the shock from the Leyden phial, a certain degree of it being requisite to overcome the resistance of the animal fibre, a violent one is given from a battery constructed with this repetition, in other words, with plates, the number of which is great, compared with the surface. For the same reason, a certain intensity of the galvanic matter will be requisite to overcome the resistance of the fluids subjected to its action, all of which are likewise comparatively imperfect conductors, and hence the same accumulation of it, from resistance in the galvanic series, will favour its action on these fluids. But in the application of galvanism to metals, as these admit it with comparatively little resistance, it is not requisite that it should be at the same pitch of *intensity*, the effect will rather be dependent on the *quantity* applied; and hence the large plates generating and affording it with more rapidity, the effect it produces on the metals, that of igniting and causing them to burn will be increased. It was found by Van Marum, what is conformable to this view, that the intensity of the galvanic fluid from a given number of plates was the same, whatever might be their size, though the quantity must no doubt be different.

It follows from this view, that with regard to the production of all these effects, a certain relation will subsist between number and surface in increasing the power, and it is even probable that this will be different with regard to all the three effects, or that with regard to each, there will be a certain proportion most favourable to each. Two of them, however that of giving the shock, and that of producing chemical de-

compositions, have been confounded, or supposed to follow the same law, and the whole has been considered under rather too general a point of view, probably from the trouble which must attend the minute investigation of the subject. It has been stated in general terms, that the power of igniting the metals is simply in the ratio of surface affording galvanism, while the other effects are in proportion to the number of plates, at least when the size of each plate is not less than $1\frac{1}{2}$ inch square.

This subject, however, has been investigated with more care, and the laws, with regard to number and surface, more accurately determined by Ritter. His researches on this point, which appear to be highly important, have not, I believe, appeared in any of the English Journals, and I have not met with them in any of the French Journals to which I have access. For the following abstract from a German Journal *, I am indebted to my friend Professor Jameson:

"*A.* Ritter constructed a pile with 1000 plates of copper, zinc, and pasteboard, moistened with a solution of common salt in a decoction of litmus and galls, (as this conducts better than a simple solution of common salt). He divided these into ten piles, each consisting of 100 plates, and connected them together, in the common way, into a single large pile. He hung on the upper plate (which was zinc) of each of these piles a leaf of gold, and began first by including 100, then 200, and 300 plates in the conducting circle. The maximum of combustion he determined by the magnitude of the perforation which the blunt extremity of the iron-wire, used in connecting the extremities of the

* Gilbert's "*Annalen der Physik.*"

pile, burns in gold-leaf attached to the *plus* side; or if the action were strong, by the size of the perforation burnt in a leaf of brass foil. This maximum, with the above arrangement, he found to be between the 200 and 300 plates; beyond these the spark, to external appearance, for some time seemed greater, but it continued to lose its energy on the gold leaf, until at length all the 1000 plates taken together, scarce yielded a trace of true combustion, and the effect of the spark on the gold leaf appeared to be only mechanical.

" The *chemical effect*, which was determined by the quantity of gas evolved from the decomposition of water in a glass tube, increased from 100 plates, pile for pile, yet always slower, and usually at 600 plates it reached its maximum; 700, 800 plates, and so forth, operated more weakly, and all the 1000 plates considerably weaker than the 400.

" With respect to the *shock*, its energy increases 100 for 100 to 1000, and then it required a strong resolution to overcome the feeling, so that its maximum, with the above arrangement, seems to be beyond 1000. From piles of the same kind, of 1500 plates, the shock was insupportable; but still no maximum could be observed.

" *B*. He erected a pile of the same magnitude, with a simple solution of sea-salt. He found the maximum of *energy of the spark* at the 200th plate; at 300 its action began to diminish, and at length the gold leaf was only mechanically affected, and more so than in case *A*. The maximum of the *chemical effect* was at 500: 1000 was not more powerful than 300. No maximum of the shock was observable.

" *C.* He constructed a pile of 2000 plates of copper, zinc, and cold concentrated solution of sal-ammoniac.

" Here the *spark* had its greatest energy or *maximum*, between 600 and 800 plates, and then from this began again to diminish.

" The *maximum of chemical action* was not to be observed within 2000 plates. It was supposed to be at 4000 or 6000 plates.

" No *maximum of the shock* was observed. It is absolutely impossible, even when the hands are dry, to bear the shock of 2000 plates. A chain of 50 persons only connected slightly, and with dry hands, was most dreadfully agitated. From analogy, the maximum will be at 18,000 or 20,000.

" *D.* He constructed a pile of 1000 plates, and moistened the pasteboard only with well-water.

" A maximum of the spark was not accurately discoverable. He places it at 100; the maximum of chemical effect was above 100 plates; the maximum of the shock between 600 and 700; at 900 and 1000 the sensation was weaker. If the hands are wetted with a solution of common salt, the maximum of sensation is between 500 and 600; if wet with solution of sal-ammoniac, between 300 and 400."

The general conclusion, it is obvious, which follows from these experiments is, that a certain law is observed with regard to the relation of surface and number in a galvanic arrangement in producing the galvanic phenomena. The power of acting on living matter is most dependent on number, so that increasing the number adds to this effect; that of producing

combustion is dependent principally on surface, so that increasing the number without increasing the surface is soon attended with a diminution of energy. The power of producing chemical decompositions is in its relation to number and surface intermediate between these. But in all of them a certain relation exists, or a certain proportion between number and surface gives the maximum, and increasing either indefinitely, is accompanied by a diminution of power. If both, however, be increased, preserving always the proper proportions, the power may probably be indefinitely increased. This law, I may observe, agrees with the preceding view, that a certain degree of intensity in the galvanic fluid is requisite to enable it to penetrate imperfect conductors. This intensity is produced by its accumulation in the galvanic pile or trough, and this accumulation is obtained by the repetition of imperfect, compared with that of perfect conducting matter in the galvanic arrangement: of course, by the repetition of the plates, between each of which the fluid or humid disc (the imperfect conducting matter) is interposed; and as from the relative conducting powers of the cuticle, of fluids, and of metals, a greater degree of intensity will be requisite to enable it to penetrate the first than the second, and the second than the third, so the maximum of effect on animal matter, in other words, of the shock, must from plates of a given surface, be at the greatest number; the maximum of decomposition of fluids at an intermediate number; and the maximum of effect

on the metals at the smallest number, compared with extent of surface.

It is a singular circumstance with regard to the Voltaic apparatus, that it does not appear to admit of an accumulation of the galvanism much beyond the extent in which that influence is generated by it. If the extremities of the apparatus are connected, the excess of power is discharged at that wire which is positive, and produces its effects on any substance interposed in the circuit. This discharge continues to proceed, but if the communication between the two extremities be suspended, it does not appear that the galvanism is much accumulated, or that after the interruption, it acts with more momentary energy than before.

Mr Wilkinson has shewn, however, that when the plates are very small, and of course the surface exposed to action in the trough inconsiderable, compared to the quantity of liquor in the cells, there is an accumulation of power, a shock from a trough of 600 plates, each half an inch square, being much more powerful at intervals of four or five minutes, than when taken at shorter intervals.

With regard to the theory of Galvanism, the first question that naturally occurs is, what is its nature? Is it the same with electricity?

In their properties, and in the laws they observe, they have a very near resemblance. The sensations they excite in animals, though not perfectly the same, are very similar; they are both capable of stimulating the muscles to contraction, and by this power are the most delicate tests of the presence of irritability. Galva-

nism, in its transition from one matter to another, is like electricity highly luminous; like it, too, it produces intense heat, and is thus a powerful agent in occasioning both chemical combination and decomposition. The conductors of the one are in general conductors of the other, while substances which refuse a passage to electricity are impervious to galvanism.

The connection of galvanism with electricity is proved to be still more intimate. Volta observed, that on applying two metals together, an arrangement from which we know galvanism to be produced, the one becomes positive with regard to electricity, the other negative, as he discovered by his condenser. On the discovery of his pile he found that the two extremities of it are in different electrical states—that connected with the more oxidable metal of the arrangement,—the zinc in the one generally employed, being *plus*, that with the other *minus*, and this has been confirmed by the experiments of Nicholson, Cruickshank, Van Marum, and others. From each extremity of the insulated pile, the electricity diminishes towards the middle, and at the central plate scarcely any signs of it can be discovered, as follows indeed from the nature of the galvanic battery. It has also been affirmed, and on the first authority, that by forming a connection with the extremity of the pile, and a coated jar, it will receive a weak charge, and that even an entire electrical battery may be charged. Volta states, that with his pile he is able to charge, not only a Leyden phial, but even a large battery in the twentieth part of a second, and nearly to the same intensity as in the pile itself; and that such a

charged battery gives sensible shocks. To give such a charge it is extremely necessary that the slightest interruptions in the communications of the conductors from the pile with the coatings of the bottle should be avoided*. The experiments of Van Marum and Pfaff on this subject, are also extremely interesting. They made the experiment on twenty-five jars, which they charged first separately, then a few at a time, and lastly all together. When the zinc was at the top of the pile, and the wire from it connected with the inside of the jar, the electricity of the inside was positive; and they found uniformly that the single jars or the batteries were charged to the same degree of intensity as the pile. They also charged the battery from different portions of the pile, and found the charge to correspond with the intensity of that portion of the pile from which it had been made. They examined the shocks given by the battery thus charged from the pile. The charge made from twenty pairs of plates was inconsiderable; that from forty was felt at the wrists, and from sixty at the elbows. At the same time these shocks were not equal to those from the pile, but only about half the strength. They lastly proceeded to ascertain the comparative effects of the common electrical machine, consisting of a plate of glass 31 inches in diameter. A single momentary contact of the conductor did not give a charge to the battery, capable of being discovered by the elec-

* Nicholson's Journal, 8vo. vol. i. p. 140.

trometer; six of these contacts gave a charge of the same intensity as that from one contact of the pile. On comparing the shocks given by the battery, from contact with the pile, and contact with the machine, they were convinced, on repeated trials, that there was no perceptible difference between the sensations or shocks from each, provided the intensities were the same *.

These experiments appear to establish the identity of the two principles, Galvanism and Electricity. To account for the slight differences between them,—the difference in the sensation received immediately from the pile, and from electricity, the galvanic influence not easily penetrating the cuticle or other imperfect conductors, and the powerful chemical effects of galvanism, compared with its low state of electrical intensity, the hypothesis suggested by Mr Nicholson † seems probable; that galvanism is electricity in a stream of great tenuity, while electricity evolved by friction is more concentrated, and is evolved as it were in successive quantities. That galvanism, if it be electrical, should be in such a state as this hypothesis assumes, seems to follow necessarily from the nature of the arrangement by which it is generated, which, consisting of a series of conductors, it is little accumulated by any substance, but must be carried off as rapidly nearly as it is produced, while, from the

* Memoir of Van Marum, Nicholson's Journal, 8vo. vol. i. p. 173.

† Journal, 4to. vol. iv. p. 243.

nature of the electrical apparatus, this does not happen, the conducting power of the glass evolving it from friction being so inconsiderable. That galvanism does exist in this state of low intensity and constant evolution, appears from the spark from conductors of a galvanic battery being so small, and unable to overcome the resistance of the air, if the points of the conductors be at a very small distance. It is established with still more certainty by Van Marum's experiments, in which a charge of a battery of 137 square feet of coated surface, of as high intensity as could be communicated by a pile of 200 pairs, was made by a single contact, while, to give a charge of the same intensity from the most powerful electrical machine perhaps in Europe, required the momentary contact to be repeated six times. This shews that the galvanic fluid must have moved in an uninterrupted stream of great velocity, while the weak charge it did give proves its low intensity. Ritter has remarked, that as the pieces of pasteboard in the pile become dry, the time requisite to give a charge is greater, so that a pile, which with pieces thoroughly wet, would give a charge instantaneously, will, when they are nearly dry, require 10 or 15 minutes.

By a galvanic series, then, it seems to be proved, that electricity is rapidly evolved and carried off, or a larger quantity for every moment of time is given out by such a series, than by the common electrical machine, while in the latter, the electricity, by its accumulation is raised to a much higher degree of intensity. Dr Wollaston, by a particular electrical arrange-

ment, contrived even to produce a stream of electricity somewhat analogous in its effects to galvanism. A silver wire, $\frac{1}{120}$ of an inch in diameter, was coated with sealing-wax, and cut through the middle, so as to expose a section of the wire. On immersing the coated extremities of these two portions of wire, at $\frac{1}{10}$th of an inch distance from each other, in a solution of sulphate of copper, and placing them in the electric circuit of a common electrical machine, the wire on the negative side had a precipitate of copper formed on its surface; an effect precisely the same with that which would have happened in the same solution at the negative wire of the galvanic battery. On reversing the direction of the current as to these wires, the copper was re-dissolved by the power of the wire, now rendered positive, while at the other, now negative, a similar precipitate of copper was formed. Other effects similar to those of galvanism were obtained *.

On the hypothesis that electricity and galvanism are the same, it remains to be determined by what cause is it evolved and put in motion in the galvanic arrangements. Two explanations have been given of this subject, one originally proposed by Volta, the other originating with the British chemists.

Volta's hypothesis rests on a fact which he proves by experiment, that "if two different metals, perfectly dry, insulated, and having only their natural quantity of electricity, be brought into contact, on removing them from that contact, they are in different electrical states; the one is positive, the other nega-

* Philosophical Transactions for 1801, p. 429.

tive." In the example of the metals now generally used in galvanic arrangements, the zinc is in the former state or *plus*, the copper in the latter or *minus*. The difference is not very considerable; it is perceptible, however; but when accumulated in an electric condenser by repeated application of the plates, becomes sufficiently strong to cause the electrometer to diverge. Electricity, therefore, is developed by the mere contact of different metals, independent of any foreign action on them; or one metal, by its contact with another, forces part of its electrity into that other, and this inequality of distribution continues while they are in contact, and no conductor is applied to them. Different metals have different powers in this respect. Volta has placed them in the following order, from his own experiments: silver, copper, iron, tin, lead, zinc, it being understood that the first causes electricity to move into the second, and those which follow it, the second into the third, &c. Some minerals, as plumbago and black oxide of manganese, and also charcoal, have a similar power.

If a series of such plates were constructed, without any intermediate substance, what would be the result? The copper commencing this series, and in contact with a plate of zinc, would yield to it part of its electricity, and the zinc, as demonstrated by experiment, would become positively charged. But if the series be continued, in other words, if another plate of copper be placed on the other side of the zinc, this action is interrupted, the zinc being in contact at each of its surfaces with the two plates of copper, two equal forces act in opposite directions, and thus destroy or

counterbalance each other. Hence the result of such an arrangement would be, that the difference in the electrical state would not be greater in the whole, than in a single pair of the plates, and would even amount to nothing if the arrangement began and ended with the same metal. An augmentation of force cannot even be attained by an alternate arrrangement of three metals, as they differ little in the same power. But if a piece of moist card or cloth be placed between the plates, in the example quoted, between the zinc plate and the second copper plate, the effect of the latter on the former is interrupted, the fluid in the card having comparatively with the metal little of this peculiar electro-motive power, or property by contact of breaking the equilibrium of electricity, does not itself check the motion, but acting as a conductor, conveys the positive electricity from the zinc to the next copper plate; and accordingly, on this addition of the moistened card, Volta finds by experiment, that signs of electricity are manifested in the series.

On these facts may be explained the evolution and motion of electricity in the common galvanic arrangements. Suppose the pile to commence with a plate of copper on an insulated base, and that over this is placed a plate of zinc, by the contact the copper becomes negative, or loses a portion of its electricity, which the zinc acquires; if a piece of moistened pasteboard be placed over the zinc, having very little of the peculiar electro-motive power, it does not counteract, or does so in so slight a degree as to admit of being neglected, the action between the pair of plates,

but operating as a conductor, a piece of copper placed above it must now acquire the same electric state as the zinc below. The pile being supposed insulated, this can be done only at the expence of the undermost copper plate, and hence it loses still more of its electricity, or becomes more highly negative, it losing as much as the other two acquires. On now placing over the second copper plate a second plate of zinc, it must acquire more electricity than the copper over which it is placed, which can be acquired only at the expence of the pieces beneath, and each of these will therefore suffer a proportional diminution; the first, or that which commenced the pile, will become more highly negative than before; the second and third pieces, which were positively charged, will have that charge diminished, and approach nearer to their natural state: the second one more so than the third; while the upper piece, which of course is the second plate of zinc, will be more highly positive. In this manner, the quantity of electricity in the uppermost plate will increase in arithmetical progression as we rear the pile, while it will be proportionally diminished at the base, and the two extremities will therefore be in the opposite electrical states, the difference being greater or less according to the number of plates; and as many degrees as the plate at the head of the column is positive, so many will that at the bottom be negative, while in the middle of the column there will be two plates in their natural state.

When a communication is made by a conductor between the two extremities, a current of electricity is established; or if a communication be established be-

tween the earth and the base of the pile, and a communication of the other extremity with conductors, the metal which yields electricity to the other receives it from the earth, continues still to give it to the other, from which it is carried forward by the contiguous fluid or humid substance, and thus a constant current, increasing as it proceeds, is established. If the pieces of card be moistened with a saline solution, or a diluted acid instead of water, the effect of the pile it is known is greater. This Volta ascribes to their greater conducting power, and he shews by experiment what proves this, that although the effects are more considerable when these liquids are employed, the tension indicated by the electrometer does not equally increase, but appears even to be the same, at least in comparing water with a solution of sea-salt. The different galvanic powers of the different metals, he supposes owing to the degrees in which they possess this electro-moving power, or to the effect of breaking by contact the electric equilibrium being greater in some than in others, zinc taking electricity from every other, and gold yielding it to the rest.

Volta, though he finds that the action which has now been described, as putting in motion the electric fluid, is greatest between the metals, finds likewise, that it exists, though in a less degree, in other substances, as in charcoal, metallic oxides, and a number of liquids: between some liquids and metals it is such as to allow of a galvanic arrangement being formed of such liquids and a single metal; and in this way is explained the construction of such an arrangement, from a metal with its different sides in contact with

diluted nitric acid and a solution of sulphuret of potassa, as has been already described. If we could discover solid substances which were conductors of electricity without having the electro-motive power, a pile might even be constructed by their medium, without the intervention of any fluid whatever *.

The hypothesis opposed to Volta's, is that which supposes the electricity in a galvanic series to be evolved in consequence of the chemical action of the substances composing it. It was undoubtedly suggested by the researches of Fabroni. These discovered some singular facts as to the mutual action of metals. He observed, that metals when pure preserve their lustre for a long time, but that their alloys are quickly tarnished, and oxidated by exposure to the air; that the contact of two metals hastens the oxidation of each; and hence, as Fabroni found, if pure metals be put in separate vessels of water, they are not altered; but if two of them be immersed in water in contact, the more oxidable one is soon loaded with oxide. The signs of electricity which are observed when two metals are separated from contact, are rather to be considered as the consequence of this chemical action than the cause; all the other phenomena, even the sensations which the metals excite, Fabroni regards as the immediate effects of the chemical action, and not as the effects of the electricity which that action evolves †. This cor-

* Report to the National Institute, translated in the Philosophical Magazine, vol. xi. p. 301. Letter of Volta, translated in Nicholson's Journal, 8vo, vol. i. p. 135., and Memoir by Volta, *Annales de Chimie*, t. xl. p. 225.

† Nicholson's Journal, 4to, vol. iv. p. 120.

rection in the theory, however, was soon made by the British chemists, and the evolution of electricity in the galvanic apparatus ascribed to the chemical action existing in the parts composing it, probably by that action diminishing the capacity for electricity, or the power of the substances to retain it, or perhaps in consequence of the motions by which it is attended.

The following is the mode in which the determination of the electrical current in the galvanic apparatus has been explained, according to this hypothesis. The first series in the pile or trough is copper, zinc and fluid; the chemical action is exerted between the fluid and the contiguous surface of zinc, and in consequence of it the electricity is evolved, or passes from the substance of the zinc to the surface acted on; the plate, therefore, becomes negative,—a state which is likewise communicated to the copper on the opposite side. The electrical current is thus determined, or it passes from the zinc through the fluid, (according to Dr Bostock, who has stated this hypothesis more fully than any other writer, by the electric matter combining with the hydrogen, which arises at the same time from the decomposition of the fluid *); it is thus brought to the next plate; were this zinc, a chemical action would also be exerted between it and the fluid, and a current in an opposite direction, by which each would of course be neutralized, would be formed; but being of copper, and the chemical action being always on the more oxidable metal, the copper merely conducts

* Nicholson's Journal, vol. iii. p. 10. 75.

the electricity, the surface of the zinc towards the commencement of the arrangement is protected, but on the other side a fresh portion of electricity is added to the current by the chemical action which is there exerted; this is repeated at each of these plates, the quantity of electricity is thus increased as the current proceeds, and when it issues from the last zinc plate of the battery must be in a positive state, while the other extremity is negative.

The difference between these two hypothesis is obvious. According to the one now stated, the electricity is generated at the contact of the humid substance with the more oxidable metal, and the use of the other metal is merely to prevent an opposite action, and determine the electrical current; while, according to that of Volta, the electricity is generated at the contact of the two metallic plates, and the fluid or humid substance, serves the purpose only of effecting a communication between the metallic pairs, so as to impel the electrical fluid in one direction.

It has been supposed difficult to decide on the merits of these hypotheses, since in favour of each of them there are certain facts of considerable weight.

The theory of Volta rests on a fact which is not controverted, that two metals, by mere contact, alter their electrical states. This is established not only by his own experiments, but by experiments which had been before made, though unknown to him, by Bennet and Cavallo *. The action of the metals in the galvanic arrangement, may therefore be such as he describes, and from the fact itself it ap-

* Nicholson's Journal, 8vo. vol. i. p. 144.

pears to be proved, what he contends for, that electricity is evolved from conductors, independent of chemical action. This being admitted, to what other cause, he observes, can it be ascribed in such experiments than to mutual contact.

It is true also, that the saline solutions, and the acids, which promote so much the generation of galvanism, are, as the hypothesis of Volta supposes, better conductors of electricity than pure water. This Berthollet remarks, was established prior to those researches by Priestley and Morgan *. At the same time, I must remark, that it does not follow from Volta's hypothesis, that their superiority in the construction of galvanic arrangements shall be precisely proportional to their superior conducting power; for, in all cases, their action in regulating the motion of the galvanic influence is in some measure counteracted by their electro-motive power; and this they may be possessed of in different degrees.

So far, therefore, Volta's hypothesis appears to be established; but, on the other hand, some facts have been stated, which have been supposed to prove, that chemical action has a share in the production of this power. The power of the interposed liquids seems in general to bear a proportion to their chemical energy; they promote the generation of galvanism, while that action is exerted, and it ceases as they are neutralized. Mr Davy has shewn, that when pure water is used to moisten the cards in the pile, scarcely any galvanism is excited; while if it hold atmospheric air, oxygen

* Statics, vol. i. p. 162.

gas, nitrous gas, or an acid in solution, the pile acts with more or less force. When we perceive the action thus promoted by substances which we know act chemically on the metals, it is perhaps illogical to disregard this, and to suppose that the difference in their effects is owing to different conducting powers communicated to the fluid. A fact of a similar kind, and supposed to be still more decisive, is, that the action of the galvanic arrangement is much dependent on the chemical nature of the surrounding medium. Major Haldane found, that when the pile, constructed of silver, zinc, and discs soaked in pure water, was placed *in vacuo*, its action immediately ceased; that in a jar of atmospheric air, it went on for a limited time; that in a jar of nitrogen gas, it did not even commence, while in oxygen gas it was more energetic; and either in this gas or in atmospheric air, the oxygen was consumed *. These facts were confirmed by Mr Davy, who farther found, that in other gases, not capable of affording oxygen, as hydrogen, or carburetted hydrogen, the galvanic action could not be excited; but that when two or three drops of nitric acid had been added to the portions of water between the metallic plates, it was immediately excited even *in vacuo* †, as it is also according to Van Marum's experiments, when a solution of muriate of ammonia is used; though even then the power is much increased by the pile being placed in oxygen gas. They appear to prove the intimate connection be-

* Nicholson's Journal, 4to. vol. iv. p. 319.

† Ibid. p. 339. 395.

tween the evolution of galvanic electricity, and the chemical action of the substances from which it is evolved.

It must still remain doubtful, however, whether these facts are altogether conclusive, since it is at least possible, that the greater power of these fluids, whether those consisting of water originally prepared with certain additions, or with additions from the surrounding medium in the course of the process, may be owing to their superior conducting, combined with their peculiar electro-moving powers. What strongly confirms this, and is altogether unfavourable to the chemical theory, is, that in many other cases, the powers of different fluids, in producing galvanism, are by no means proportioned to their chemical action. Thus, next to acids, the solutions of pure potassa, of muriate of soda, and muriate of ammonia, are most effectual in promoting it; yet they by no means exert any very great chemical energy. If we compare the action they do exert, with that of other substances which likewise act on metals, but which generate less galvanism, or with the rapid action of acids, and compare their exciting galvanic powers, it will appear that these are in no proportion, but that the exciting powers of the solutions of these salts, are greater than what such a theory would suggest. With regard to potassa, for example, it exerts so little chemical action on the metals, that, according to Van Marum, their polish is not even impaired *. The same conclusion will follow from the comparative action of the different acids. Sulphuric acid, diluted, has much less power than muriatic or nitric acid in

* Nicolson's Journal, 8vo. vol. i. p. 180.

exciting galvanism. Yet its chemical action on the metals in a galvanic arrangement is as energetic.

When to these facts are added the consideration, that the principle of Volta's theory is an established truth,—that metals, by mere contact, and independent of any chemical action, break the electric equilibrium, —and that in an arrangement such as the galvanic pile or trough, it is demonstrable, that from such a property the electricity must increase from the commencement towards the termination of the arrangement; there are perhaps sufficient grounds to conclude, that it is the preferable one, and that on this cause the evolution of galvanism depends. If the facts which have been stated to shew the connection between the production of galvanism and chemical agency, and the consideration which may be added, that electricity of which galvanism is undoubtedly only a particular form, is evolved by chemical processes, be regarded as sufficient to prove, that such an agency must have at least a certain share in the production of galvanism; yet it is probably only a subordinate cause, or serves merely to modify the other. Our knowledge, however, of this agent, is probably too little advanced to admit of a perfect theory being established; the subject will no doubt be farther prosecuted; for its operations promise to throw much light on the processes of chemistry, and to add greatly to our command of chemical powers.

WIGAN

NOTES.

Note A.

I have remarked in the text, that the doctrines of chemical affinity, which were formerly considered as established, have been materially modified by the speculations advanced by Berthollet. A general statement of these I have incorporated in the enumeration of the laws of chemical attraction, without illustrating them minutely, or engaging in much discussion with regard to the evidence on which they rest, as this would have involved details, with which the reader of an elementary system must be supposed unacquainted. But as the subject is highly important, while at the same time the different parts of it are not free from obscurity, it will not be uninteresting to consider it more fully. The additional illustrations and observations which I conceive necessary, I shall state in the order referred to in the text.

A. (p. 75.) The change of properties from chemical combination is its most important effect, and is therefore an interesting subject of inquiry. Newton, to whom we are indebted for

the first just views of chemical affinity, supposed the properties of a compound to be derived from those of its elements, and from this principle deduced his singularly acute conjecture, that water contains an inflammable ingredient. Stahl maintained the same opinion, or taught that the properties of compounds are intermediate between those of their constituent parts. As in the progress of chemical observation, however, many cases occurred which appear in direct opposition to this principle, and as the doctrine itself, at least as advanced by Stahl, rested in a great measure on hypothetical views, it was gradually relinquished; and for some time chemists have been satisfied with stating merely the general fact, that in many cases of combination the properties of the bodies combining are not much changed, while, in other cases, the change is striking and complete, without endeavouring to refer this difference to any principle. Berthollet, in the course of his speculations, has in some measure connected these facts, assigned causes for the peculiarities that are observed, and thus given a general theory of the change of properties from combination, of which it may not be uninteresting to give a brief connected view.

One great cause by which the chemical properties of bodies must be materially modified by their combination, is the diminution which saturation produces in the strength of their affinities. Hence the chemical action of a compound must be less energetic than that of its simple elements; and this constitutes, accordingly, in many cases, the change from combination, in what are named the chemical properties of a body or the peculiar actions it exerts. It is well exemplified in the neutral salts, which have much less activity as chemical agents, and less tendency to combination, than either the acids or alkalies of which they consist.

At the same time, this is often modified by another circumstance, the condensation which attends combination, and which sometimes weakens the action of substances; in other cases adds to its force. The chemical action, for example, of substances existing in the aëriform state, are in some measure counteracted by their elasticity. Hence, if an elastic ingredient

enter into a combination, in which it exists in the liquid state, the action it exerts may be more increased by this condensation, than weakened by the affinity, which is of course exerted to it by the substance with which it is combined in the compound. Of this we have an example in the acids; as in the nitric acid, where the chemical action, arising from the affinities exerted by the oxygen existing in it, is in many cases more energetic than that of oxygen in its aërial form. On the other hand, where condensation from chemical action is carried so far, that the elements in combining pass to a solid state, the cohesion thus acquired will concur with the diminution of their attractive forces from saturation, in limiting the affinities they exert, or in counteracting the affinities which may be exerted by others towards them; and hence such a compound will be less susceptible of chemical action than its constituent parts. Thus we perceive, how, from the influence of condensation in different degrees, and from the effect of saturation on affinity, the chemical properties of bodies may be changed. The same condensation, it is obvious, may also modify other chemical properties, and we accordingly find it do so. Thus, we perhaps cannot produce an example, where a compound is more volatile than the mean volatility of its ingredients. In the greater number of cases, from the condensation the elements experience, it is more fixed. By the same condensation, the mechanical condition must be changed; and to the new arrangement of particles which an energetic combination occasions, may be ascribed the change in colour, transparency, and other physical properties, which often attends chemical union.

Another circumstance, from which arises much of the alteration which bodies suffer in their properties from combination, is, that, where opposing or incompatible properties exist in substances, which, when they are combined to saturation, must be mutually destroyed, as in the characteristic property of acids of reddening vegetable colours, and the equally characteristic one in alkalies of changing these colours to a green. One of these cannot be predominant but from the other having been

impaired; and an equality of force gives rise to a state in which the characteristic properties neither of the one substance nor of the other are discoverable. This is well illustrated in the combinations of acids with alkaline bases, and the formation either of neutral compounds, or of compounds with acid or alkaline properties as either ingredient predominates.

The theory, therefore, may be maintained, that the properties of substances combining enter with them into the combination, and would always be discoverable in the compound, were it not for accompanying circumstances, by which they are modified or disguised, and apparently new properties acquired. Incompatible qualities are neutralized; affinities become weaker from saturation; they are also in some cases impaired, in others favoured, by the condensation and mutual penetration which the bodies suffer; and from the same condensation, the properties arising from the mechanical constitution of the bodies must be changed.

From these observations may be deduced the general rule, that where energetic affinities are exerted, or where substances having opposing properties are united, the properties will be much changed; but where the affinity exerted has not been energetic, or where the substances combined are such as agree in the general assemblage of their qualities, the properties of the compound will not differ far from the mean of those of its constituent parts, or of its more active ingredient. One of the most striking examples of chemical combination with little change of properties, is in the solutions of salts in water. In this, the affinity effecting the solution does not appear to be a powerful one, for there is little condensation, and it is easily overcome by the application of heat, and, such as it is, its force is in some measure spent in counteracting the cohesion of the solid; and accordingly in this, the only property that suffers alteration is the form. Of the combination of bodies which have few opposing properties, the metals furnish an example which illustrates the general theory. They agree in the possession of a certain range of properties; and the individual metals differ rather in the degree in which these belong to them,

than in having peculiar or characteristic ones, which might often be incompatible. Accordingly, when they are combined, the compounds they form have still the general metallic qualities, varied only, but in general not very materially changed, so as to be far from the medium of those of the substances uniting; at least, not more than may be accounted for by the change of the force of affinity, and in the density which arise from the combination.

Even in those cases where more energetic affinities are exerted, and where substances with opposite characteristic properties are combined, we may often trace the properties of compounds, from those of their constituent parts. For example, if we compare the salts which ammonia forms with the acids, with the salts which the other alkalies or earths form, we observe that the former are distinguished by their volatility, a property undoubtedly derived from their base. In like manner, as Berthollet has remarked*, we have illustrations of this in the sparing solubility of salts, composed of ingredients which have a great tendency to solidity or fixity, compared with those which have tendencies of an opposite nature, as in the phosphates, oxalates, tartrates and sulphates, compared with the muriates, the nitrates, and the acetites, and in the earthy compared with the alkaline salts. In the properties of these salts, he observes, we find "an exact correspondence with the supposition, that their insolubility depends on the natural disposition of their elements, increased by the condensation arising from the affinity which unites them†."

Yet I must remark, that though these and similar facts are favourable to the theory, or accord with it, there are many for which, on the same principles, it would be difficult to account. To take an example which Berthollet himself has partly stated: Lime and magnesia form salts which are deliquescent: the

* Chemical Statics, vol. i. p. 259.

† Ibid. vol. i. p. 260.

salts, on the other hand, which potassa and soda form with the same acids, have no such property; yet from the theory the reverse might be expected. Potassa and soda are deliquescent substances; lime and magnesia are not. If the property, therefore, remain in the compound, it ought to be apparent in the salts having the two former for their base, not in those formed by the latter; nor is there any evident cause why in the latter, or the salts of lime and magnesia, such a property should exist. Berthollet, in comparing these two earths in this respect with barytes and strontites, which do not form deliquescent salts, ascribes the difference to "the influence of the "capacity for saturation;" by which probably is to be understood, that as magnesia and lime saturate a larger quantity of acid than these bases do, the property of deliquescence may be derived from the acid, which, in the deliquescent salts that these earths form, the muriates, for example, has a strong attraction to water. But this larger quantity of acid which these bases condense, is supposed by Berthollet himself to denote a stronger attractive force which they exert; and of course, this ought both to neutralize more completely any property of the acid, and produce a compound with more density or tendency to cohesion, and ought hence to prevent deliquescence, if this property were derived from the acid. Besides, the contrast of these two earths with potassa and soda in this respect, is much stronger than the contrast of them which Berthollet has exhibited with barytes and strontites; since the latter, at least so far accord with the theory, that if they do not produce deliquescent salts, they are not themselves deliquescent, which potassa and soda are. These alkalies also differ much less from magnesia and lime in the capacity of saturation; soda indeed differs very little. And, lastly, ammonia, which has an attraction to water unquestionably as great as soda or potassa, is a similar example to which the solution does not apply; for it does not produce deliquescent salts, and yet, in capacity of saturation, it is inferior to lime.

Besides these, many other examples might be quoted. Thus muriate of lime is deliquescent. Fluate of lime is so far from

being so, that it is altogether insoluble in water; yet as both acids have a strong affinity to water, and as they do not appear to differ much in the force of the affinity they exert to that base, there is no apparent cause for this difference. It will be found equally difficult to account for the peculiar properties of the alkaline carbonates. The whole class of salts, indeed, might be passed under review, and as many would be found unfavourable as favourable to the theory; proving, therefore, so far at least, its deficiency.

Facts also might be stated from other classes of compounds, which appear irreconcilable with the theory. To select one example: Arsenic is a metal easily volatilized. When combined with oxygen, it forms in the first proportion a compound, in which the principle of the theory is sufficiently exemplified, this compound being more volatile than the metal itself. But when still more oxygen enters into the combination, a compound is formed, which is perfectly fixed; or, in this example, a substance, by combining with the base of an elastic fluid, not only renders it fixed to a certain extent, but the entire compound, instead of approaching to a medium volatility, becomes even less volatile than the ingredient of it which is most fixed; nor is there any such condensation from the combination as will serve to account for this.

There are also properties observed to be acquired by compounds, for the production of which it would be difficult, on the preceding principles, to give any explanation. Suppose, for example, as Berthollet is disposed to maintain, that the characteristic properties of acids depend on their oxygen, from what modification of condensation, or any other circumstance, can arise the most characteristic quality possessed by all of them, that of changing the vegetable colours to a red, a property not observed in oxygen? Or from whence can the opposite property of the alkalies, that of changing the vegetable colours to a green, derive its origin?

Yet it must be admitted, that a slight circumstance may give rise to apparent difficulties, and that in such cases we cannot be assured that all the modifying circumstances are precisely known.

We can scarcely expect more perhaps in the theory, than that it shall accord with the greater number of facts. If there are some which appear to be not comprehended under it, or even to be in opposition to it, this probably may arise rather from the difficulty of the investigation, than from the principle itself being false. It accords with many phenomena; and it is an important acquisition, if we can refer to a general principle, luminous and fertile in applications, what must otherwise be received merely as an ultimate fact.

B. *(p. 81.)*—The production of heat and cold from chemical action is no doubt referable to the ultimate law, that by combination the capacities of bodies for caloric are changed, the extent of the change being appreciable by experiment. But there is a less abstract view, as referring to the more immediate causes, under which the subject may be considered, which Berthollet has stated in considering change of temperature as an effect of chemical action, and of which an account may be given, rather more ample than could be introduced into the text.

The effect of chemical combination is condensation, or there is a mutual penetration, in consequence of which the compound occupies less volume than its constituent parts. Now condensation is always accompanied with an evolution of caloric, as is established with least ambiguity in the rise of temperature produced by reducing the volume of an elastic fluid by mechanical pressure. The effect must undoubtedly be the same, when the condensation is the effect of chemical action; and accordingly, the connection between these was so obvious, that it could not escape observation. It was remarked, that where two fluids combine together, forming a compound fluid, there is an increased density; and this is as invariably accompanied with a rise of temperature.

It could not fail, however, to be also remarked, that the degree of heat produced in different cases of chemical action is by no means proportional to a certain degree of condensation, but in some cases is much greater, as measured by that condensation, than in others; and the opposite change, or the produc-

tion of cold, although it is always connected with enlargement of volume, is likewise not found, in the different cases in which it occurs, to be proportional to that enlargement.

The cause by which these are modified, so that the proportions are not observed, is the transition of form which so frequently accompanies combination; a fluid, in consequence of it, becoming solid, or an air becoming fluid, or the reverse of these changes taking place. A change of form is of itself, and independent of any alteration of density, invariably accompanied with an evolution or absorption of caloric; the absorption taking place when the substance becomes fluid or gaseous, and the evolution when it passes from the aëriform to the fluid, or from the fluid to the solid state.

In chemical action, therefore, we have two causes producing change of temperature, and modifying each other,—condensation, and change of form; the effect of the former being to produce heat, and that of the latter, according to the kind of change, to produce either heat or cold: the one therefore will sometimes counteract, sometimes concur with the other.

If, for example, a fluid act with energy on a solid, condensation will be the immediate effect of the combination, and so far will be productive of heat. But if, at the same time, the solid, in consequence of that action, pass into the liquid form, or be dissolved, the effect of this is an absorption of caloric, or production of cold. As the latter is the more powerful cause, it generally prevails; and in solutions, actual cold is the result. But this is not always the case. In some energetic combinations, considerable heat even is produced, although a solid passes into the fluid state; as in the solution of desiccated potassa or soda by water; and still more in the solution of these, as well as of some of the earths in an acid, the condensation from the combination being more than sufficient to counterbalance this opposing change of form.

In like manner, if the result of a combination be the evolution of a substance in the aërial state, this change of form will likewise counteract the effect from the condensation otherwise resulting from the combination, and lessen the quantity of heat

that would have been evolved ; yet still the condensation from the combination may be sufficient to furnish, not only the caloric for the constitution of the gas, but to render a portion sensible, and raise the temperature, as happens in the action of a concentrated acid on an alkaline carbonate, where the acid is condensed with perhaps a portion of water by the alkali ; or in the action of nitric acid, or diluted sulphuric acid, on a metal, where the oxygen of the acid or water passes into a still denser state of combination with the metal, and this oxide again passes into a similar state with the acid.

Or, if we take the reverse of these cases, the conclusions are similar. If the result of the chemical action is the transition of a substance from the aërial to the fluid, or from the fluid to the solid state, this transition will co-operate with the increase of density which attends the combination, and will cause more heat to be evolved than that increased density by itself could have produced. We find too, that heat, more or less considerable, arises from the combination of two fluids ; because even although the combination be feeble, there is always some degree of condensation, and there is no change of form to produce an opposite effect ; and where the condensation is considerable, as in the combination of sulphuric acid or alkohol with water, the rise of temperature is very observable.

This principle may equally be applied to explain the production of cold. This happens generally in the solutions of solids in fluids ; and here two causes operate to produce change of temperature. The body dissolved passes to the fluid form, and, in conformity to a general law, this change is attended with an absorption of heat. But the effect of its combination with the solvent is to produce condensation by which heat is evolved. In these solutions, however, the combination is comparatively weak : the condensation, therefore, is not considerable, and is not sufficient to counteract the absorption of heat from the liquefaction of the solid. Hence the solution is attended with reduction of temperature.

The following is the general summary of this theory as stated by Berthollet himself. " The immediate effect of all com-

bination is an elimination of caloric. This effect may be disguised in weak combinations, by the changes of bulk occasioned by the passage from the solid to the liquid state, or from the liquid to that of elastic fluid ; but when they are energetic, the effect of combination with respect to caloric always overcomes that of the accidental dilatation of volume. Still there is not in combinations the correspondence between the changes of dimensions and the evolutions of caloric which is observed in insulated substances. Hence it would be an error to establish it as a general principle, that dilatation is always accompanied with reduction of temperature ; and it would be another to pretend that condensation constantly produces heat. These effects may sometimes balance each other, or the excess of one above the other may produce the result *."

The only deficiency, perhaps, in the theory, is, that the distinction is not very clearly stated between the operation of the two causes of density,—that from combination, independent of change of form, and that from the change of form itself, which is the consequence of the combination. In attending to this subject, it might appear at first view that these are similar, or must ultimately have the same effect with regard to temperature ; that there is no necessity for attending to them distinctly, but that we have only to examine the total variation of density, from whatever cause it may have arisen, and endeavour to connect it with the change of temperature which is observed.

For example, when a body changes its form, its density is altered. In passing from the aërial to the fluid, or from the fluid to the solid state, it becomes more dense, and at the same time part of the caloric it contained is evolved. If, therefore, a substance in combining with another becomes solid, why, it might be asked, should the theory be encumbered, with taking the density from this cause into distinct consideration ? May it not be connected with the density arising from the combination, independent of the change of form, and thus the total condensation be measured and regarded as the cause of the evo-

* Chemical Statics, vol. i. p. 180.

lution of caloric? Or, in the opposite case, where in a solution a solid is rendered fluid, this fluidity must be accompanied with a diminution of density: the combination at the same time occasions a greater or less increase of density; but it seems an unnecessary subtilty to speculate on the effect of each: it appears sufficient merely to consider the actual change, or the degree of alteration in density which has resulted from the one of these circumstances having overbalanced the other.

It will be found, however, that this apparent deficiency in the theory of Berthollet, arises merely from an imperfect statement he has given of it, and that it is strictly necessary to keep in view the changes of form which may occur in combinations, independent of the alterations of density by which these changes may be accompanied. For by change of form new relations to the principle or cause of heat are acquired, from the new arrangements of the particles which are produced; and these are independent of the alterations in density which may happen at the same time. In estimating, therefore, the absorption or evolution of heat when a body changes its form, we can never be guided by the difference of density in the body in the one state compared with that in the other, for these are never proportional to each other. Hence appears the necessity, in giving the theory of change of temperature from chemical action, of considering distinctly the two circumstances of change of density from the combination, and change of form from it; and it is by this distinct consideration of these two circumstances, that the preceding view is able to explain the fact, not otherwise accounted for, the connection of the production of heat in chemical combination with increase of density, and of the production of cold with diminution of density, while at the same time they are not proportional to each other. It must also perhaps be admitted into the theory, that in different bodies a change of density, to an equal extent, will be productive of different degrees of heat or cold, from the different relations they have to caloric; and although it is so far satisfactory to trace the immediate causes, the phenomena

must perhaps be ultimately referred to the changes of capacity, as ascertained by experiment.

c. *(p. 85.)* No part of the doctrines which Berthollet has advanced is more important than what relates to the influence of external circumstances on the exertion of affinity. They are comprehended under the general proposition, that affinity is not an uniform force, varying merely in its intensity, as exerted by different substances, but that it is much modified by several causes, chiefly by Quantity of Matter, Cohesion, and Elasticity.

Of these, quantity of matter is undoubtedly the most important, since it influences so much the operation of the others, and the doctrine with regard to it affords several important corollaries. The following are a few of the facts referred to in the text, as those by which the truth of the principle Berthollet has advanced, that quantity of matter within the sphere of action adds to the force of the affinity which that matter exerts, is established.

" I have kept," says he, " an equal quantity of potash, and of sulphate of barytes, in a small quantity of boiling water. The potash had been prepared by alkohol, and contained no carbonic acid: the same served for the following experiments. The operation was performed in a retort, and consequently in communication with the air; and it was continued until the mixture was desiccated: the residue was washed with alkohol, which dissolved the potash, and after that with water, which also produced an alkaline solution, the alkali of which I saturated with acetic acid; after which, by evaporation, the solution yielded crystals, possessing all the characters and qualities of the sulphate of potash. Whence it appears, that the sulphate of barytes was partially decomposed by the potash, and that the sulphuric acid was divided between the two bases*."

Now, since the barytes is considered as having a stronger attraction to sulphuric acid than potassa, and since, under the

* Researches into the Laws of Chemical Affinity, p. 8.

same circumstances, pure barytes decomposes with facility sulphate of potassa, we have here an example of a superior, being overcome by what is regarded as a weaker, affinity.

" Sulphate of potash," says Berthollet, " having been submitted to a similar experiment with an equal weight of lime, and the dried residue having been treated with alkohol, an alkaline solution was produced : and a part of the residue dissolved in water, and yielded a small quantity of sulphate of lime along with the sulphate of potash *." Here the conclusion is similar, for sulphate of lime is decomposed by potassa, yet we find that sulphate of potassa can also be decomposed by lime. In the same manner, oxalate of lime was decomposed by potassa, phosphate of lime by potassa, carbonate of lime by potassa, and sulphate of potassa by soda. In all, it is evident, " that the bases which are supposed to form the strongest combinations with the acids, may be separated from them by others, whose affinities are supposed to be weaker, and that the acid divides itself between the two bases. It also appears, that acids may be partially separated from their bases by other acids, whose affinities were supposed to be weaker ; in which case, the base is divided between the two acids †." And it follows from these experiments, " that when a substance acts on a combination, the subject of combination divides itself between the two others, not only in proportion to the energy of their respective affinities, but also in proportion to their quantities. The two substances which act on the combination ought to be considered as two antagonist forces, which act in opposition while they act on, and share between them the subject of the combination in proportion to the intensity of their action ; which intensity depends on the quantity of the substance, and on the energy of the affinity : so that the effect increases or diminishes according as the quantity increases or diminishes ‡." This is the correct expression of the general law.

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* Researches into the Laws of Chemical Affinity, p. 9.

† Ibid. p. 11. ‡ Ibid. p. 14.

Some facts similar to those which have now been quoted, were even formerly known to chemists. Nitrate of potassa, for example, is decomposed by sulphuric acid, the acid combining with the potassa, and the nitric acid being expelled; yet nitric acid is capable of again decomposing sulphate of potassa, and reproducing a portion of nitrate of potassa. In the same manner, muriate of soda is decomposed by sulphuric acid, and muriatic acid expelled, yet sulphate of soda is again decomposed by muriatic acid. These facts, apparently anomalous, were classed together by Bergman, as forming what he named Reciprocal Affinity, and an ingenious hypothetical explanation of them given approaching to the truth, and which, previous to the researches of Berthollet, was generally received.

While the properties, both physical and chemical, of a compound, were regarded as in a great measure independent of its elements, and as arising from the peculiar arrangement which constitutes its integrant particles, it was supposed that this compound might have an attraction to an additional proportion of one of its ingredients, precisely as it might have to any other substance; and on this supposition was founded Bergman's explanation of reciprocal affinity; the affinity of the compound to one of its ingredients concurring with the affinity exerted by any substance to the other ingredient, and thus causing a partial decomposition. In the instance quoted, and which had been best observed, the sulphate of potassa was supposed to have an attraction to an additional quantity of sulphuric acid; when acted on by the nitric acid, therefore, two conspiring affinities operate,—the affinity of the salt to an additional proportion of sulphuric acid, and the affinity of the nitric acid to its base; and by these two it is supposed the decomposition is effected. The decomposition must necessarily be partial, since, when the sulphate of potassa has received, in the progress of the decomposition, the quantity of sulphuric acid to which it has an affinity, there remains only the affinity of the nitric acid to the potassa, which of itself is unable to prevail.

Notwithstanding the ingenuity of this explanation, there can be little doubt but that this case of reciprocal affinity is mere-

ly an example of the participation of a substance between other two having an attraction to it. Potassa has an attraction both to sulphuric acid and nitric acid. If it be acted on by both, therefore, they will divide it in the ratio of their quantities, and the intensities of their affinities. The intensity of the affinity of the sulphuric acid, aided at least by the force of cohesion, is superior; but that of the nitric acid, when it is present in considerable quantity, is still able to abstract a very sensible portion of the potassa, and hence arise the results. The effect of this last affinity can only be counteracted by adding a large quantity of sulphuric acid, and by favouring the elasticity of the nitric acid by the application of heat. We may then render the decomposition of the nitrate of potassa nearly complete.

Instead, however, of considering the subject under this point of view, it has been conceived that the doctrine of reciprocal affinity, as stated by Bergman, may be applied to the explanation of those experiments, from which Berthollet has deduced the general principle, that quantity influences the force of affinity. Thus, to take as an example the first experiment which he has brought forward, that in which sulphate of barytes is decomposed by potassa, instead of ascribing it merely to the simple affinity of the potassa, aided by its quantity, it might, in conformity to Bergman's hypothesis, be explained on the supposition, that sulphate of barytes has an attraction to an excess of base. When that compound, therefore, is exposed to the action of potassa, there are, according to this hypothesis, two forces concurring to its decomposition: first, the affinity of the potassa to its acid; and, secondly, its own affinity to barytes. From these a part of the sulphate of barytes may be subverted in composition, its acid transferred to the potassa, its barytes to the remaining portion, which of course escapes decomposition; and a similar explanation may be given of the other experiments.

It might be observed, too, with regard to these experiments, that the phenomena which ought to be produced, according to Bergman's view, are precisely those which ought also to be

observed in conformity to that of Berthollet. Thus, according to Bergman, the decomposition must always be partial; for as it is partly owing to the affinity which the compound exerts to one of its ingredients, it must cease when that affinity is satisfied, and cannot possibly proceed until the whole of the compound is destroyed. Hence also none of the ingredients of that compound can be separated in a pure state. But, according to Berthollet's view of the subject, the decomposition ought equally to be partial; for, in proportion as it proceeds, or as a portion of one of the principles of a compound is abstracted, the remaining portion must be held by a stronger force, the affinity of the other ingredient to it being augmented by the increase in the relative quantity of that ingredient. The more sulphuric acid is attracted by potassa from the barytes in sulphate of barytes, the more powerful ought the affinity of the barytes to the remaining acid to become, from the increase in its relative quantity; and it is difficult to conceive, that where the affinities are so nearly of the same force, and at the same time so energetic, potassa in any quantity whatever should be capable of abstracting the acid entirely from the base, or that, in an experiment of this kind, barytes should be obtained pure. The effect of cohesion in some cases indeed intervenes, and evolves the principle of a compound pure and isolated; but this can have no effect in the present case, as the sulphate of barytes has more cohesion or less solubility than the barytes in its pure state.

Yet though Bergman's explanation may thus be applied, it must be admitted to be less simple and direct than that given by Berthollet, and that, as extended to the preceding facts, it is altogether gratuitous. In the particular cases to which Bergman himself applied it, the decomposition of sulphate of potassa by nitric acid, or of sulphate of soda by muriatic acid, there were some grounds for the conclusion, that these salts were capable of exerting affinities to an excess of the acid they contain. But we have no similar proofs in the preceding experiments of an affinity of sulphate of barytes to barytes, or carbonate of lime to lime; or that such affinities, if they do exist, are sufficiently powerful to produce the effect. The hypothesis has

no advantage over the other; and it is merely a limited and hypothetical view of phenomena, which are referable to a more general principle.

Indeed, if examined closely with the admission, which, from the state of the fact, necessarily must be made, that these affinities of a compound to an excess of either of its ingredients are not limited to a certain fixed proportion, as Bergman supposed, but are indefinite, at least to a certain quantity, it will be found perhaps ultimately not to differ essentially from the more simple statement, that the force of affinity is modified by quantity of matter, or in any combination differs in its strength, in different proportions.

Besides, there are a number of chemical phenomena to which the hypothesis of Bergman cannot be applied, but which accord with the principle established by Berthollet, and must indeed be considered as proofs of its truth.

Thus, no fact must have been more frequently observed by the practical chemist, than that in adding water to a number of metallic salts, to those of mercury or antimony for example, a transparent solution might be obtained, which, if more water were added, became turbid from decomposition. It never suggested, however, the just conclusion, and was indeed scarcely taken notice of. Yet what proof can be given more simple and decisive of the truth, that quantity influences the force of affinity? or on what other principle can the phenomenon be explained? It deserves too, to be remarked, that in such decompositions, there is no limitation in the progress of the decomposition; no successive formation of two or more determinate compounds. The addition of a small portion of water has no decomposing effect; if a little more be added, the transparency will still remain; with a farther addition, it will begin to be impaired; by continuing the addition, the metallic oxide is deprived of more and more of its acid, becomes more insoluble, and renders therefore the liquor more turbid; and by the affusion of a sufficient quantity of water, the whole of the acid nearly may be carried off. Of course, the decomposition cannot be referred to the metallic salt having an attraction to an excess of

oxide; for, granting such an affinity, it ought soon to be satisfied, and not require the addition of so large a quantity of water, if that water did not, by its quantity, influence the affinity; and it may, besides, be continued, until the substance consists of almost nothing but oxide: it must therefore be admitted as a proof that quantity adds to the force of affinity.

The whole class of facts too, (stated in the text p. 82.), which gave rise to the statement of the partial and empirical law, that attraction is in the inverse ratio of saturation, afford proof of the justness of the principle equally conclusive, as do those numerous facts, which prove, that precipitates from chemical action are scarcely ever pure, but retain a portion of the substance with which they were combined. And, from considering the whole of these phenomena, we find them connected and accounted for on the principle, which, from the very nature of affinity, cannot be regarded *a priori* as improbable, that the affinity exerted by a body to another is increased by the quantity of it brought within the sphere of action.

An objection might occur to this principle, from the consideration that chemical affinity extends to no perceptible distance, but is exerted between two bodies only at the point of apparent contact. The effect of this, it might be supposed, must be to place limits to the influence of relative quantity on its exertion; for any quantity beyond that which can exist within the sphere of contact, can apparently exert no operation. If a particle of sulphate of barytes be on every side in contact with particles of potassa, what additional force can be gained from an additional quantity of potassa, which must be without the sphere of action? This objection, however, may be obviated, by considering the manner in which quantity operates. Suppose two bodies, A and B, to be presented to each other, the particles of each within the requisite distance will combine together in that proportion in which they will be mutually saturated. Suppose A to be the one which is in larger proportion, its mass will continue to operate, and, even if there be no successive application of it to B, from the motion attending the combination, its uncombined or unsaturated particles will take part of the parti-

cles of B which have entered into the combination; so that the whole particles of B which have been attracted by A, instead of remaining combined with part of it, in the proportion in which saturation takes place, will be diffused through the mass; and hence, by an increase in this mass, there will be an addition to the force of affinity.

No law with regard to chemical affinity is more important than that now illustrated, not only from its direct influence, but as modifying the operation of the other circumstances by which chemical action is influenced.

Cohesion is the second principal circumstance pointed out by Berthollet as influencing chemical action. The relation of this power to chemical attraction could not altogether escape the notice of chemists, but their views with regard to it were limited. They observed, that when it was exerted with much force, it prevented the solution of bodies, which, if it were overcome, could be dissolved with comparative ease; but they considered it in general as acting only in these extreme cases: they did not observe the gradations in its action, as an antagonist to chemical attraction, nor its more important effects in placing limits to combination, or determining it in fixed proportions. These are the points of view under which it has been regarded by Berthollet. In the theory of its influence which he has given, are included some established doctrines; but these were not before so distinctly expressed; they were not combined; and there is considerable novelty in some parts of it, particularly in shewing that the phenomena which used to be referred to particular powers of adhesion or physical affinity, probably arise from chemical attraction, balanced by the power of cohesion; in illustrating the cause of the limits to solution from the decreasing ratio with which the force of affinity is exerted, while the cohesion remains uniform; in observing the influence of cohesion in liquids, in which it was always regarded as too inconsiderable to have any effect on combination; and in explaining its agency, in determining combinations in fixed proportions.

In the first place, from considering cohesion and chemical

attraction as antagonist powers, and comparing the effects which arise from them when they are exerted in different degrees of intensity, Berthollet traces a variety of shades of combination more or less intimate, and, in consequence of this view, refers to one principle those varieties of action, which have been considered as produced by peculiar forces, named variously, Attraction of Adhesion, Capillary Attraction, Physical Affinity, and Hygrometric Affinity. These he regards as mere varieties of chemical attraction, balanced more or less by cohesion. "The distinction attempted to be established by some philosophers between chemical affinity and physical adhesion is without foundation; for the effects which they attribute to the latter, depend on the same cause as those which are owing to affinity, and are only different in the energy of the reciprocal action compared with the resistance opposed to it *."

Thus, if in a solid substance, the cohesion exceed the affinity exerted to it by any liquid, the solid will remain unaltered as to its form or properties, but may still present some shades of union with the liquid. The affinity may indeed be so weak, or the cohesion so strong, that the fluid will even not adhere to the surface of the solid, as in the example of a drop of water applied to a polished metal; but in other cases this adhesion takes place, and extends along the surface, contrary even to the specific gravity of the fluid, especially where that surface is great, proportioned to the quantity of liquid, as in tubes of narrow diameter, producing the phenomena which have been referred to what has been termed Capillary Attraction. From a still stronger affinity, the liquid may be imbibed by the solid, without however the force being sufficiently energetic to separate the particles from their state of cohesion. This happens in hygrometrical phenomena, which were ascribed to this cause by Saussure. If it be a little more powerful, or the cohesion less strong, the latter power may be so far weakened by the affinity of the liquid imbibed, that the solid is reduced to pow-

* Chemical Statics, vol. i. p. 18.

der, as is exemplified in the slaking of lime by water. Sometimes, though not sufficiently powerful to reduce the solid to its ultimate particles, it is sufficiently so to hold small masses of it suspended for a considerable time, notwithstanding the difference of specific gravity, as is observed in various precipitates. And, lastly, if the affinity is still more powerful, and the quantity of fluid sufficiently large, the cohesion is altogether overcome, and the particles of the solid are dissolved by the liquid.

In this case a new series of phenomena commences, in which we perceive the relation of cohesion to the former modifying circumstance, quantity of matter. Chemical action is exerted, not only in the ratio of the attraction of one body to another, but likewise in the ratio of their quantity ; and hence in solution the power exerted by the liquid, or, to speak more correctly, the reciprocal tendency to combination in the solid and liquid diminishes, as the solution proceeds. The affinity may at first have been sufficiently strong to overcome the cohesion of the solid ; but the action of the liquid, in consequence of the law with regard to quantity of matter, becoming weaker as it approaches to saturation, it may, after a certain period, be so far reduced in force, as to be unable to produce this effect, when of course the combination must cease.

We have thus a clear view of the nature of solution, and of the causes by which it is limited. Formerly the general fact was merely stated as an ultimate one, that a fluid dissolves certain quantities of different solids, without the cause of these limits to it being distinctly pointed out. This is done in the view now taken of the relation between cohesion and chemical affinity. When a fluid is poured on a solid, suppose water on a salt, it first overcomes the cohesion of the solid by the attraction it exerts to its particles ; hence these particles are detached and combined with the fluid, or the solid is dissolved. But when the cohesion of the solid can thus be overcome by the affinity of the fluid, why should the solution not proceed until every intermediate consistence between solidity and fluidity is attained ? The reason is, that the attraction of the fluid, in conformity to the law which arises from the effect of quantity,

diminishes as it approaches to saturation. It, therefore, in the progress of the solution, arrives at an equilibrium with the power of cohesion in the solid, and then, it is obvious, the solution must cease. Hence also the quantity of matter dissolved is increased, by raising the temperature, as this diminishes the force of cohesion.

Lastly, a peculiarity in Berthollet's view of the effect of cohesion is, that it is regarded as influencing the progress of combination, insulating substances, at certain stages of it, by separating them from the sphere of action, and thus in a great measure determining the proportions in which they combine. Thus, from the influence of cohesion, a salt may crystallize in a neutral state, from a liquid in which there is an excess either of acid or alkali, the cohesive attraction being exerted with greatest force at the point of neutralization, where there is the greatest condensation, and being sufficiently powerful to overcome the affinity of the remaining acid or alkali, at least if the excess is not considerable. In the same manner a combination may be insulated at the point of neutralization, if the compound formed at that point have much tendency to cohesion, and a precipitate of the compound in that state be thrown down, though there may be still present an excess of either of its ingredients. This belongs, however, rather to the consideration of the causes of the limits to chemical combination.

The effect of Insolubility is precisely similar, and indeed insolubility is to be regarded merely as the result of cohesion, in relation to the liquid in which its effect appears. Accordingly, if in a chemical decomposition, the substance evolved by the decomposing substance be insoluble, being immediately withdrawn, the decomposition proceeds with rapidity, and may be complete, as in the decomposition of muriate of lime by potassa. But if, on the other hand, the substance eliminated be soluble, as it remains within the sphere of action, it continues to oppose the action of the decomposing agent, and the substance to which each has an attraction is soon participated between them, in proportion to their affinities and quantities. It is thus that in the action of lime on sulphate of potassa, the

decomposition of the latter must soon cease ; for the potassa, when separated from the acid, remains in solution, and opposes the farther action of the lime, the affinity of which is diminishing, and which, in the present case, is also counteracted by the cohesion acquired.

Elasticity. The influence of elasticity on chemical action scarcely requires any other observations than what are stated in the text. It is obvious, that as it places the particles of matter at considerable distances, it must prove an antagonist to chemical attraction, the operation of which extends only to distances that are inconsiderable, and that hence it must oppose the combination of substances possessing it, and likewise facilitate the decomposition of a compound, one or both of the ingredients of which have a disposition to take the elastic state.

But there is a theoretical question connected with it of some interest, especially as the facts to which it refers appear anomalous, and even contrary to what these views of the operation of elasticity would lead us to expect : it is what relates to the effect of a high temperature in promoting the combination of substances possessed of elasticity. Two elastic fluids or airs, having even strong mutual affinities, may be mingled together without their particles entering into combination, owing to the repulsion between the particles of each, so that they are placed beyond the sphere of chemical attraction. But on applying to the mixture a temperature equal to ignition, as by introducing an ignited spark, or an electric discharge, the particles in some cases through the whole mixture are instantly united, their caloric evolved, and an intimate combination formed, the result of which is frequently a substance which does not remain in the elastic state ; in other cases, a stream of sparks requires to be kept up ; yet in these also the combination, though proceeding more slowly, is still complete. Yet, in conformity to the cause that has been assigned for their not combining, it apparently follows, that the application of a high temperature, by increasing the elasticity, and augmenting the distances between the particles, must counteract instead of facilitating the combi-

nation. And since the fact is, that it does facilitate it, how is this to be reconciled with the theory?

I shall transcribe the explanation which I gave of this singular circumstance in my former Treatise on Chemistry: "When a spark is introduced into the mixture of two gases having an attraction to each other, the point on which it falls is immediately heated to an intense degree; whence an expansion, proceeding from that point as from a centre, is produced; and this expansion, by the pressure it must occasion on the surrounding particles, will cause them to approximate, and thus to unite. The whole effect is instantaneous, and it is upon the sudden operation that it depends. Were the caloric to be slowly introduced, the expansion would be slowly extended over the whole mass, and would be equal throughout; the particles, therefore, would be still farther separated. But a single point being merely heated to a high degree, while the surrounding particles remain at their usual temperature, the expansion from the former must suddenly press upon the latter, much more quickly than the temperature can be communicated. These, therefore, instantly approximate within the verge of chemical attraction, and thus the union must be effected. After it has taken place, more caloric is rapidly, but successively, extricated by the combination itself, which will of course produce a similar effect on the remaining mass, till the combination is completed. There are some gases, however, from the union of which so little caloric is extricated, that the introduction of a single spark is insufficient, and therefore a stream of sparks must be kept up *."

Precisely the same explanation has been given by Berthollet in his late researches. "Compression, by causing the moleculæ of two gases to approximate, augments their reciprocal action; it may be carried to a point at which it causes combination: now that part of a gas which first receives the heat experiences a dilatation which is greater in proportion as the

* Elements of Chemistry, p. 96.

heat is more intense ; it compresses, with a strong effort, those parts of the gas which have not yet received the same degree of temperature ; by that means it determines them to combine ; but the caloric which abandons this combination, and which raises it to a much higher temperature, produces, by the tension which is the consequence, a much stronger re-action, so that the part which at first only dilated, is itself compelled to enter into the combination. The caloric therefore only causes, by the dilatation of one part of the gas, a compression on that which is less heated, but the total of the effect is owing to the sudden approximation of the moleculæ produced by the combination *."

This explanation is much confirmed by the interesting experiment made by Biot, that of producing, by mechanical compression suddenly applied, the combination of two aërial bodies, which at moderate temperatures do not otherwise combine, the combination being accompanied with phenomena precisely similar to those which appear when they are united by an ignited spark ; the mixture of oxygen and hydrogen being combined by the strong and sudden compression applied in an air-gun, with a violent explosion and flash of light †. Mr Northmore has also shewn what is conformable to the same view, that oxygen and nitrogen can be combined by compression, and that other elastic fluids, by the same cause, exert reciprocal actions, which under a common atmospheric pressure and temperature are not observed ‡.

An important corollary flows from the consideration of the extensive influence of the preceding circumstances on the exertion of chemical attraction,—that it cannot be affirmed, in any case, that bodies have no attraction to each other. There are examples of substances which we cannot combine together, as oil and water, water and quicksilver, potassa and oxygen, &c. ; and from such facts, which are numerous, it was regarded as a

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* Chemical Statics, vol. i. p. 222.

† Annales de Chimie, tom. liii. p. 321.

‡ Nicholson's Journal, vol. xii. p. 212. Ibid. p. 368.

law, that between some bodies no chemical attraction exists. The fallacy of this conclusion must be obvious, and the principle may even be admitted as *a priori* extremely probable, that all bodies exert mutual attractions between their particles.

That the circumstance of bodies not being capable of being brought into combination is no proof of the entire absence of any mutual affinity, is obvious from the consideration, that combination is in no case the simple result of the exertion of attraction, but of attraction prevailing over cohesion, or elasticity, and difference of specific gravity; and therefore the circumstance, that combination cannot be effected between bodies, may arise as much from the predominance of these forces, as from the entire absence of reciprocal attraction. If we pour alkohol on sea-salt, no sensible portion of the salt is dissolved; but it is obvious that this may arise from the affinity which the alkohol does exert to the salt, not being sufficiently strong to overcome its cohesion and specific gravity; and we cannot employ a high temperature to lessen these opposing qualities with effect, because the alkohol is so expansible a fluid, and so much disposed to volatility, that we would lose as much in force on the one hand, as would be gained on the other. A similar explanation applies even where two liquids cannot be combined together; for although in bodies in this state cohesion is much weakened, it still exists, and may be sufficient to counteract a weak affinity. We observe it in some cases to place limits to combination, as in the example of sulphuric ether and water, the latter being capable of combining with about one-tenth only of the former; and it may in other cases, where the affinity is still weaker, as is probably the case in the example of oil and water, be able, together with the difference of specific gravity, to resist attraction effectually, and prevent any combination. In the case of a solid and aëriform substance, as in the example given of potassa and oxygen gas, the obstacles to combination are still more powerful, being the cohesion of the one, and the elasticity of the other, and the circumstance which will diminish the former, that is, a high tem-

perature will augment the latter. Hence we may expect in this kind of relation still more examples of substances refusing to combine, but evidently without the conclusion following, that these substances have no mutual attraction. Lastly, in elastic fluids, the elasticity may frequently counteract sufficiently a weak affinity, even under the circumstances by which their mutual action is promoted.

If this reasoning required any illustration, it might easily receive it, from taking a few examples of substances which are combined with much difficulty, and supposing either their affinity to have been a little weaker than it is, or the counteracting circumstances somewhat more powerful. Thus gold is combined with difficulty with oxygen, and only in indirect modes. It is obvious, that if the affinity between them had been a little weaker, or the cohesion of the gold somewhat greater than it is, even these indirect modes would have failed; and in this case the erroneous conclusion might have been drawn, that these substances had no mutual affinity whatever.

It is difficult to conceive of attraction otherwise than as a force possessed by every particle of matter, and exerted to every other; and the theory is evidently superior, which supposes its attraction to be prevented from being efficacious, by the interference of extraneous forces, than to suppose, that between certain substances it is altogether wanting, especially since in all cases the action of such forces can be demonstrated, at least to a certain extent, which may be sufficient to account for the effects.

We shall find too, in the next note, sufficient reason to believe, that the mutual affinities of compounds are the modified affinities of their constituent principles, though in many cases such affinities in the elements are not observed to be exerted, from the opposing circumstances which the combination removes being sufficient to counteract them.

n. (p. 107.*)* The opinion appears to have been generally received by chemists, that the attractions exerted by a compound belong to its integrant parts, and are not derived from

the affinities of its constituent principles, farther than that the combination itself, which gives rise to the compound, is derived from the exertion of these; and when they were not aware of the great influence of external circumstances in modifying affinities, this must have appeared most probable. The attractions of a compound are totally dissimilar to those of its principles, as in the example of water and its two elements. It combines with substances to which they appear to have no attraction, and it refuses to unite with others with which they form intimate combinations. The difference between the affinities of a compound and its elements, is indeed so general, and often so complete, that it must have been difficult to conceive how it could arise from any modification of the elementary affinities. Hence the notion was adopted, that when two substances combine together, the attractions of the compound they form are exerted, not from its ultimate elements, but from its integrant particles, are peculiar to them, and arise rather from their configuration than from any modification of their elementary parts; that when water exerts attractions, these are from the particles of the water as such, and not from the ingredients of which it is composed.

We may perceive the extensive applications which may be made of the speculations of Berthollet on chemical affinity, when we find that the opposite view may be maintained with perhaps more probability,—that the attractions of compounds are merely the modified attractions of their constituent principles. This is the view which he has given; and to distinguish such affinities, he has named them Resulting, as discriminating between them and the elementary affinities, which the compound may likewise exert. As chemical attraction is reciprocal, when a simple substance exerts an affinity to the entire compound, this also belongs to the class of resulting affinities, or it is composed of the affinities it exerts to the constituent principles of the compound, while, if exerted to one of these principles, it is elementary.

The following, although not all of them explicitly stated by Berthollet, may be regarded as the general principles of the

doctrine ; and in their application they afford an admirable view of many chemical phenomena.

If the attraction of a substance to one of the principles of a compound be much superior to its attraction to the other, in this case an elementary affinity will be called into action, and the compound decomposed. If the attraction exerted be nearly equal to each, a resulting affinity will be established, and the substance exerting it will combine with the compound ; and this will even happen where there is an inequality, if not very great, in the attractions it exerts to the principles of the compound, as the affinity exerted by the one of these principles to the other is a force the effect of which is to maintain the combination, to counteract therefore the elementary, and favour the resulting affinity. Lastly, when an elementary affinity is exerted at first, as it must become weaker in the approach to saturation, it will at length not exceed in force the affinity exerted to the other principle of the compound, an equilibrium will be established, and the action will terminate in the exertion of a resulting affinity. I propose to add in this note a few illustrations on this subject, from individual substances which could not well be admitted into the text.

Sulphuric acid is a compound of sulphur and oxygen, ammonia of hydrogen and nitrogen. When ammonia and sulphuric acid are presented to each other, they combine ; and this, according to the common opinion, is from an attraction exerted by the particles of the ammonia to those of the acid. But, according to the theory now stated, when oxygen and sulphur have combined together, their affinities do not become dormant, but are only modified by the state in which they exist in the combination. When hydrogen and nitrogen combine, a similar modification of their affinities results. Each of these elements too, are supposed to have affinities to each of the others, in conformity to the principle, that all bodies have mutual attractions ; and hence the attractions which the two compounds, the sulphuric acid and the ammonia, exert, are not attractions which may be said to belong specifically to them, arising from the figure, magnitude, or any other quality of their integrant

parts, but are the elementary affinities, modified by the conditions under which the elements exist.

Water, in dissolving a neutral salt, acts by a resulting affinity, or by the attractions it exerts to the principles of the salt, modified no doubt by the attractions they exert to each other. But if its attraction to one of these principles be much superior to what it is to the other, especially where the affinity between them is not very strong, both which circumstances are found in several of the metallic salts, the affinity it exerts is elementary, and the salt is not dissolved, but decomposed.

Nitric acid is a compound of oxygen and nitrogen, and, in combining with potassa, is supposed to act by an affinity which results from the affinities of these elements. The reciprocal action of potassa, is also composed of its affinities to the principles which constitute nitric acid. Both therefore are resulting; and when exerted, they effect the combination of nitric acid and potassa. But the elementary affinities of nitric acid may also be exerted. Thus, when poured on a metal, the metal does not exert an attraction to the entire acid, but to its oxygen. This is therefore an elementary affinity; but when it is so far satisfied, the attraction of the metal to an additional portion of oxygen being nearly equal to its attraction to nitrogen, at least when that attraction is aided by the attraction of the oxygen to nitrogen, it exerts an affinity to the entire acid, with which the partially oxidated metal now combines. In this case, the elementary pass into resulting affinities.

This, in conformity to the general principles already stated, affords a beautiful view of the theory of the action of acids on metals. Metals may be conceived to have an attraction both to the oxygen of an acid and to its base, but stronger to the former than to the latter. Hence a metal exposed to the action of an acid, first attracts a portion of oxygen, but its affinity to this principle diminishing as it approaches to saturation, comes at length not to be greater than its attraction to the base of the acid, and then the entire acid enters into the combination. Hence the law observed, without exception in metallic solutions, that a metal must be oxidated before it combine with an

acid. If its affinity to oxygen is too weak to decompose the acid, being still weaker to the base it cannot in its state of cohesion exert a resulting affinity; and if previously oxidated, this lessening its cohesion, and at the same time bringing its affinity to the base to an equality with the affinity it has to oxygen, it hence combines with the entire acid.

Much of the evidence for this theory of resulting affinity, must rest on its being clearly shown, that the circumstances proved to exist in combinations are sufficient, from their known operation on chemical affinity, to account for the differences between the affinities of compounds and those of their constituent parts. This has been done by Berthollet, with much ingenuity, and, I should be disposed to conclude, with success.

Thus, it is obvious, as has been already stated, that the chemical action of substances diminishing in proportion to their saturation, resulting affinities must in general be less strong than elementary affinities. But this again is always modified by other circumstances attending the combination, which will either concur with it, and still farther weaken the affinity, or which, on the other hand, may counteract it, and render resulting affinity even more energetic.

Thus the action of a substance depends not only on the energy of its affinity, but also on the quantity of it within the sphere of action. If an elastic substance, therefore, is condensed in a combination, so as to exist in the liquid state, it derives from the combination the advantage of acting in a larger mass, and also the removal of the obstacle of elasticity. At the same time, this is diminished by the saturation it experiences from the combination; though in many cases this is much less in the resulting affinity than the augmentation of energy acquired by the condensation. Potassa, by any affinity it exerts on oxygen or on nitrogen, is unable to overcome their elasticity, or form any combination with them; but when they are condensed in their combination in nitric acid, it unites with them with rapidity. Thus, also, carbonic acid in its elastic state, is, with regard to many substances, less energetic in its action than when condensed by combination with water. To

this is to be ascribed the general energy in the action of acids, and the almost universal chemical agency of water.

If, in like manner, a substance by combination pass from the solid to the liquid state, although it may lose something in the energy of its action by the saturation it suffers, this may be more than compensated for by the advantage it gains by losing its cohesion, and its affinities may be more numerous and more easily exerted. Sulphur at a common temperature does not attract oxygen; but, when combined with potassa, so as to be soluble in water, the solution easily condenses oxygen gas; a fact which may be ascribed entirely to the fluidity of the sulphur at this temperature, though it is in part also perhaps owing to the affinity exerted at the same time by the potassa to the oxygen.

If, on the contrary, a substance by combination pass from the liquid to the solid state, this will add to the diminution of its affinity from saturation. Potassa and nitric acid are separately soluble in alkohol, but nitrate of potassa is insoluble, owing, no doubt, partly to its cohesion, and partly to the diminution in the force of the affinities of its elements, by their mutual saturation. It is still soluble however in water, as its constituent parts are more soluble in that fluid than in alkohol.

In applying the theory to particular facts, all these circumstances must be kept in view, or we must not conclude that the advantage gained in strength of action will be proportioned to the degree of condensation in an elastic ingredient, or to the fluidity acquired by a solid, but to these modified by the saturation they at the same time experience. As, on the other hand, the diminution of energy may be greater than would arise from the saturation alone, if cohesion or elasticity were not acquired; or may be less if the opposite states are the result.

The affinity of a substance which combines with a compound, concurs with its elementary affinities to preserve its composition, or resist decomposition. Hence the acids are not so easily decomposed by substances exerting an attraction to their oxygen when they are combined with any base, as when they are in their free state; and even water, by its affinity to

nitric acid, resists to a certain extent the decomposition which the acid is liable to suffer from a high temperature.

It is an important advantage of this doctrine, that it affords a satisfactory explanation of those anomalous cases of chemical action, which have been classed under the name of Disposing Affinity. On this subject it is unnecessary to add to the illustrations given in the text.

E. *(p.* 115.*)*—That part of the speculations of Berthollet which relates to the causes of the proportions which bodies observe in entering into combination, is in some measure obscure; and as the subject is interesting, I have thought it necessary to consider it at more length than I could do in the text.

His views on this subject are altogether original. That in some cases bodies combine in every proportion, in others only in one proportion, and in others in two or three determinate proportions, were formerly stated merely as ultimate facts, nor was any theory proposed by which they might be reconciled, or brought under one principle. This has been done by Berthollet; and though, from the difficulty of parts of the subject, the explanations may sometimes appear rather vague or obscure, the general theory is probably just, nor can it be uninteresting to the philosophical chemist.

It rests on the principle, that affinity is a force disposed to operate between bodies in all proportions, and tending to unite them together; that therefore any limits which are opposed to its exertion, must arise from the operation of external forces, and that it is only by these that determinate proportions are established.

This will be illustrated most clearly by considering its application to the facts, as I have arranged them, in reference to the general law. 1st, Some bodies, I have observed, combine in every proportion; 2dly, in some the combination is unlimited to a certain extent, beyond which it cannot proceed; 3dly, there are cases in which two bodies can be combined only in one proportion; and, lastly, in many cases, two or three determinate proportions are observed.

First, there are cases in which combination is perfectly unlimited. In these, therefore, we perceive the operation of the principle assumed, and that we do so, is owing to the circumstances which modify affinity either not being present or operating with little force. When two fluids combine together, little or no limit is opposed to the combination, either by cohesion or elasticity in either of them; and when the result of the combination is a substance still existing in the fluid state, in this case also either of these forces is not exerted to any extent. Hence there is little obstacle to the combination at any stage of it; the attraction is still exerted whatever may be the relative quantities of the bodies, and they combine in every proportion. This is sufficiently illustrated in the combinations of the liquid acids with water, or in the combination of water and alkohol. Yet in some cases where the affinity is weak, the remaining cohesion in liquids and the difference of specific gravity may limit the combination, as in the example of sulphuric ether, of which water cannot dissolve above one-tenth of its weight.

We may next trace the effect arising from these circumstances in determining the proportions of combinations; and this will be done with most simplicity in that variety of combination where it is unlimited to a certain extent, beyond which the power is limited.

The solution of a salt in water, illustrates sufficiently the effect of cohesion in thus limiting combination. It dissolves in all proportions to a certain extent, at which the solution ceases. In this case we have in opposition two forces, cohesion and affinity. At first the latter predominates, and part of the solid combines with the fluid; but in proportion as the solution proceeds to saturation, the affinity is weakened from the influence of quantity, and at length becomes inferior to the cohesive force; at this point, therefore, the combination ceases. But if the cohesion of the solid is weakened by the application of heat, the combination may be carried to a still greater extent; and if we could raise the temperature sufficiently high to overcome entirely the cohesion of the salt, without at the same time communicating elasticity to the water, they might be made to

combine in every proportion. There are accordingly some salts in which this can be effected,—salts which require no great heat to melt them, and which at the same time have a strong affinity to water, so as not to be weakened sensibly by the heat which is necessary. At a certain temperature, combinations of these with water in every proportion may be obtained.

The effect of elasticity in determining the proportions of combinations, may be illustrated from the solution of an elastic fluid or air in any fluid, suppose water. The affinity of the water to the air is sufficiently strong at first to overcome its elasticity; but from the influence of quantity it becomes weaker as the combination proceeds. This however is gradual and progressive, and therefore, to a certain extent, the power of combination is unlimited. But it ceases when the elasticity of the air is capable of counterbalancing the affinity, and the combination cannot be carried beyond this, but by the application of strong pressure, by which the elasticity is counteracted, or by the application of cold, which has the same effect, though this last has its limits, from augmenting at the same time the force of cohesion in the water.

The metals, in combining together, afford an illustration of the effect of fusibility and specific gravity in determining proportions. Two metals having an affinity to each other, and not differing much in these properties, will combine in every proportion, while the difference, if considerable, will limit the combination to certain proportions.

But the variety of combination most frequent, and at the same time most difficult to account for, is that where it is in no part of its progress unlimited, but takes place invariably in one or more determinate proportions. It is explained by Berthollet on the following principle.

The effect of every combination is condensation of the substances combined. In weak combinations the condensation is inconsiderable: no effectual obstacle is opposed therefore to the progress of the combination; and hence it may take place in every proportion. But in combinations produced by a stronger affinity, the condensation is more considerable, and it

may be so much so as to oppose the farther combination, and cause it therefore to assume a determinate proportion.

This will most probably happen at that point where the condensation from the combination is greatest; for experiment shews, that in combinations there is always a proportion of the substances from the union of which the greatest condensation arises. Now at this point the power of cohesion will be exerted with greatest force; and according to its energy, the compound will pass from the more rare state of its ingredients, whether aërial or fluid, to a more concrete or solid form. An interruption will then take place in the progress of the combination, or it will be fixed at the proportions at which this happens; for the attraction of cohesion now exerted, will oppose an obstacle to any farther combination of its constituent parts, and that with more or less force, as the force of cohesion acquired is greater; and it will also withdraw the product from the sphere of attraction. Thus the general law of affinity is interrupted; because an obstacle which arises from its own action opposes the progress of its exertion.

A very satisfactory proof of the justness of this theory is, that if the exertion of the force of cohesion is counteracted, so that the separation of the compound at a certain stage of the process does not take place, no phenomena occur marking a determinate combination in one proportion more than in another. If an acid and an alkali be largely diluted with water, so that the compound which they form in any proportion will be retained in solution, we find them unite in every relative quantity in which they can be presented to each other; the acidity will diminish as the proportion of alkali is increased; and, on the other hand, the alkaline power is infeebled as the proportion of acid is augmented, while there is a middle term at which each is neutralized; but in all these stages there still exists a combination. They do not combine, therefore, in determinate proportions; and a compound with such proportions is only obtained by the force of cohesion acting with more force at a certain stage of the combination, and causing its separation.

This separation will in general happen at the point of neu-

tralization, at which the properties of bodies are mutually altered, and their condensation probably nearly equal, and at the greatest; at least it will happen so where the elements of the combination have nearly the same disposition to solidity; for "the insolubility which causes the precipitation, belongs to the natural qualities of each of the elements, increased by the condensation they experience." But if one of these has a greater tendency to this state than the other, its tendency will rather regulate the combination, or the separation will take place in that proportion in which there will be an excess of this ingredient. This principle explains the formation of saline compounds; it explains why the determinate combination takes place generally in that proportion in which there is mutual saturation or neutralization, and why it sometimes happens with a proportion in which there is an excess of one of the ingredients. The former will be the case where the ingredients of the saline combination have nearly an equal tendency to solidity; the latter, where the tendency of one to this state is greater than that of the other, as is exemplified in the tartrates and oxalates.

At the same time it must not be supposed, that in such combinations the principles cannot combine in other proportions. This was supposed indeed to be the case; and when facts were found incompatible with such a supposition, they were endeavoured to be explained by farther supposing, that a compound might have an attraction to one of its ingredients; might be capable of combining with it in an additional determinate proportion; and that thus other compounds might be formed than merely the one for the formation of which there appeared to be the greatest tendency. In this way were distinguished among the salts two combinations, one neutral, and one with an excess of acid; and these were supposed to be determinate, as in the sulphate and super-sulphate of potassa, or the phosphate and super-phosphate of lime. The neutral combination was conceived to be the immediate result of the union of the acid and base; and the acidulous salt the result of the union of the neutral salt, with an additional proportion of acid. But this explanation is hypothetical, and is merely an indirect mode of

accounting for the formation of compounds, which admits of a solution more easy, and more conformable to the laws of combination. There can be little doubt, but that, although there is in every combination one proportion in which the condensation and tendency to cohesion are greatest, and at which, therefore, there is the greatest tendency to separation; yet there may be combinations of the same elements in other proportions, determined by weaker degrees of condensation, or of the force of cohesion; and that by the regulation of circumstances such combinations may be obtained. It appears, that in many saline combinations, though there is a tendency in the ingredients to unite in a certain proportion, yet if presented to each other in different proportions, they still combine in these, and thus unite in many proportions; nor is this limited to two determinate proportions, as was conceived. Sulphuric acid and potassa, if the separation of the compound, at any stage of the combination, be prevented by a sufficient quantity of water being present, may be combined in every proportion, though there is only one proportion in which the properties are mutually neutralized; and such compounds, with an excess of one ingredient, may even be crystallized. Thus Berthollet, by dissolving an acidulous sulphate of potassa in water, and crystallizing it by successive evaporations, obtained each time crystals, diminishing in the excess of acid, until at length the neutral sulphate crystallized. Sulphate of soda presented the same results; and he has also shown, that various combinations can be formed of phosphoric acid and lime *.

We have thus traced this effect of condensation in limiting combination to certain proportions, on substances presented to each other in the liquid form. We have still to observe the effect of this cause on combinations of substances in the aërial state, this involving some peculiarities distinct from the preceding statements. Its effects are more considerable, because

* Chemical Statics, vol. i. p. 267.

the degrees of condensation from combination are much greater.

When elastic fluids are mingled with each other, though they may exert a weak mutual attraction, by which they are at least prevented from separating, yet their elasticity is an obstacle to their energetic combination. When favoured, however, by circumstances, they unite intimately, and the proportions of their combination will be determined by their condensation. It will generally take place in that proportion in which the condensation is greatest, for the same reason that the combination of fluids takes place at the state of greatest density. It proceeds towards that without any obstacle, and it is arrested at it, because the acquired density or tendency towards cohesion is unfavourable to the farther combination of either of the ingredients; and as this condensation is proportionally much greater than in other combinations, a more fixed proportion will be observed, as there will be a greater obstacle to the combination of the elements in other proportions. We do not, therefore, in the mutual actions of these aërial fluids, find progressive combinations, as in the salts, but they at once pass into combinations which are uniform or with little variation.

Thus the constituent principles of water, two elastic fluids, in whatever relative quantities they may be mixed together, unite only in that proportion which forms water. The condensation at that proportion is so great as to determine the combination; and the density and tendency to cohesion of the resulting compound immediately separates it from what is superfluous in the proportion of either ingredient. It may happen, however, that where the condensation is less, combinations in more than one proportion may be formed, according to the quantities of the ingredients presented to each other, or the operation of other circumstances. The combination will be established at one proportion by a certain degree of acquired density, but this may not be sufficient to insulate the compound. It may therefore be capable of combining with an additional proportion of either of its ingredients. This is the case in the combinations of oxygen and nitrogen, which take place in three

proportions. Lastly, when the reciprocal action is not strong, and does not give rise to great differences in the degree of condensation at different stages of the combination, the proportions may vary from slight variations of circumstances, as is observed in the carburetted, and perhaps also in the sulphuretted hydrogen gases.

In the combination of an elastic fluid with a liquid or solid, the condensation is greater in proportion as the attraction between them is strong, and is sometimes so great as to establish fixed points of saturation: in other cases, the solid combines with successive proportions of the elastic fluid, to the point at which the elasticity or the cohesion cannot be farther overcome by the affinity; and this species of gradual progression in the combination of a solid with an aëriform body, there is reason to believe frequently takes place, where it has been too hastily concluded, that determinate proportions were observed, as in the combinations of the metals with oxygen.

In those cases, where the solid or liquid, in combining with an air, passes into the aëriform state, limits are placed to the combination by the cohesion of the liquid or solid. And sometimes a more uniform proportion is established in these combinations, especially when they are effected at a high temperature; or, in consequence of the mutual affinity exerted, the solid passes to the aëriform state, and the combination may then become subject to the laws which regulate the combinations of elastic fluids, the condensation which results from it again insulating it at a certain proportion. Sulphur, for example, may first enter into a progressive combination with oxygen, until it has combined with such a quantity, that elasticity is communicated to the compound, which fixes the combination at that proportion forming sulphureous acid gas. But this will obey the law observed in the reciprocal action of elastic fluids; and if the temperature be suddenly raised, it may again combine with oxygen gas, and the progress of this combination will be interrupted at the point of greatest condensation, when sulphuric acid is formed.

Such is the view which Berthollet gives of the limits of com-

bination. The causes he assigns must operate to a certain extent; and if the explanations shall be found not always perfectly precise, this may perhaps be ascribed rather to the difficulty arising from the complication of the subject, than to any deficiency in the principle of the theory. Facts which are not fully explained, or which are even in opposition to what the theory would lead to expect, may undoubtedly be adduced. Berthollet, for example, remarks, that salts are disposed to crystallize in the neutral state, and, of course, to have the combination insulated and fixed at that state; but that where either ingredient has a much greater tendency to cohesion than the other, the compound may crystallize with an excess of that ingredient: and he gives us an example, which sufficiently accords with this principle, the combinations of tartaric acid or of oxalic acid with potassa, in which, as the acid is the substance most disposed to cohesion, there is observed a disposition always to crystallize with an excess of acid. But if we apply the same principle to other salts, we find few facts to accord with it; on the contrary, they sometimes appear contradictory to it, as in the examples of the compound of boracic acid with soda, or phosphoric acid with soda, both of which are disposed to crystallize with an excess of soda, though the acid is in each of them the ingredient which has the greatest tendency to cohesion, and has also less affinity to the water from which the compound salt crystallizes. And a number of similar examples might be given. We might also perhaps find, in the explanations which are given of the causes of the determinate proportions observed in the combinations of elastic fluids, a degree of obscurity and vagueness; and be able to select facts not precisely conformable to what the theory might suggest. Yet some weight must be allowed with regard to this, and other similar speculations on the difficult subject of affinity, to an observation well expressed by Berthollet, in reference to this very subject. "I am far," says he, "from pretending, in the comparison of the phenomena which I analyze, there may not be some which do not answer to the conditions I assign to them; but, in the explanation of phenomena to which a great

number of properties contribute, we must not expect to be able to determine all the causes which act, and which may lead to modifications in the results: the number and agreement of these results may, however, be sufficiently great to shew the principles from which they are derived, particularly when they are established on general principles, which cannot be controverted, and which have the advantage of connecting phenomena with those general principles which appeared to be independent of them *."

F. *(p.* 131.*)*—There can, I believe, be little doubt of the truth of much of Berthollet's theory of complex affinity, that the decompositions usually ascribed to the predominance of elective attractions, arise from the exertion of extraneous forces, principally those of cohesion and elasticity. To confine the illustration to an example he gives: "If a solution of sulphate of potash be mixed with a solution of muriate of lime, the lime brought into contact with the sulphuric acid will be more powerfully influenced by the force of cohesion than the potash. It is therefore a force in addition to those which pre-existed, and determines the combination of the sulphuric acid with the lime, and the precipitation of the new compound." In like manner, the force of elasticity, especially when aided by heat, may determine the combination of the two principles of two compounds mixed together, which have the greatest tendency to assume the elastic state, and thus give rise to an exchange of principles, which in the old theory was ascribed to the relative forces of attraction.

A strong presumptive proof that this view is just, is, that in the usual order of elective affinities, superior forces have been ascribed, among the acids, to those which form salts having the greatest tendency to cohesion, as the sulphuric, the phosphoric, tartaric, and oxalic; and among the bases, to those in like manner which form the least soluble compounds, as lime,

* Chemical Statics, vol. i. p. 264.

barytes, and strontites; and in the very exceptions in the order of the strength of affinities of these acids and bases, we find, that where weaker affinities have been ascribed to them, it has been in those cases where they form soluble salts. "Lime, magnesia, strontites, and barytes, form insoluble salts with carbonic acid. All the soluble salts of these earths, mixed with alkaline carbonates, produce an exchange, from which result the formation and precipitation of an earthy carbonate. Barytes forms an insoluble salt with sulphuric acid: therefore, whenever a solution of a sulphate is mixed with that of a salt of barytes, there will be a precipitation of sulphate of barytes. As the sulphate of lime is but little soluble, and consequently much disposed to precipitate, lime decomposes all the soluble sulphates to that term at which the precipitation is stopped by the solubility of the sulphate of lime. The sulphate of lime being much more soluble than the sulphate of barytes, the salts of barytes, which are more soluble than the sulphate of lime, decompose it *." The same relations may be traced among the metallic salts, as in the decompositions produced by the mixture of the soluble salts of silver or lead with the alkaline or earthy sulphates and muriates; and even where the force of cohesion is not exerted on any of the parts of the combination with such effect as to give rise to precipitation, still, when favoured by the evaporation of the liquid which has been the medium of action, the superior affinity will always be found to have been ascribed to the constituents of that salt which is first separated by crystallization, or which, in other words, is less soluble. Thus, in all these cases, decompositions arising from the separation of substances, in consequence of their insolubility in the liquid in which chemical action was exerted, have been ascribed to predominance of affinity.

In like manner, those acids which have the greatest tendency to assume the elastic state, have been considered as exerting the weakest affinity, because they are more easily separated

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* Chemical Researches, p. 167.

from the combinations in which they exist, though their power of saturation proves them to be possessed of energetic affinities; and the facility observed in the decomposition of their compounds, is rather to be ascribed to that volatility, in consequence of which, when another acid is added, and a participation of base begins to ensue, the volatile acid is withdrawn, and no longer opposes resistance to the action of the other.

For the same reason, in decompositions produced by heat, the weakest affinity among the alkaline or earthy bases, is in all the tables of elective attraction ascribed to ammonia; and among the acids the most powerful attractions are assigned to the sulphuric and phosphoric, which are the most fixed.

Relative quantity of matter, or the proportion of one substance to another, has an equal influence in determining these combinations; and Berthollet has shewn by experiment, that in mixing compound salts, where cohesion does not interfere with much force, a predominance of attraction may be ascribed to either acid and base, according to the proportions in which the substances are mixed together. Thus, when two parts of muriate of lime and one of nitrate of potassa were mixed, muriate of potassa was obtained by crystallization; but when equal weights of nitrate of potassa and muriate of lime were mixed, the first product by crystallization was nitrate of potassa. From the result of the first experiment, it would have been concluded, that in these salts the divellent were superior to the quiescent affinities; from the result of the second, the conclusion would have been precisely the reverse *. It is likewise shewn, what must be of much importance in practical chemistry, that in cases of this kind, where external circumstances do not operate with much force, there is a succession of combinations determined by the proportions, degree of solubility, and mutual action of the salts, and different from each other, so that an error would be committed if we should

* Chemical Researches, p. 169.
Chemical Statics, vol. i. p. 70.

suppose that the products of successive crystallizations in such mixtures will be the same as the first.

From these facts, there can be little room to doubt of the great influence of cohesion, elasticity, and proportion, in giving rise to the phenomena of single and double elective attractions; and it is needless to add to these illustrations, and to those given in the text.

But I am not certain if the opinion which Berthollet maintains, that these phenomena are to be ascribed entirely to these forces, and in no respect to differences in the forces of affinity of the bodies concerned, is altogether just. The subject is difficult and obscure, but it is important; as much so indeed as any part of the doctrines of chemistry; and it may be interesting to examine the grounds on which his opinion rests.

Its primary proposition is, that if three or four substances are brought within the sphere of action, whether they be altogether uncombined, or whether, in the case of three substances, two of them may have been previously combined, or in the case of four, they may have been united, two and two,—in any of these cases, if no extraneous forces operate, their affinities will be reciprocally balanced, so as to form one combination; and binary combinations will be produced solely from the exertion of other powers. "When two bases act in opposition on an acid, this acid divides itself, or rather divides its action, in proportion to their respective masses: if there be two acids instead of one, and if no separation result, either by precipitation or crystallization, both acids will act equally in both bases in proportion to their respective masses. If each of the acids be previously combined with a base, and the solutions of their salts be mixed, the sum of the reciprocal forces of the acids and alkalies will be the same as before." In mixing potassa, sulphuric acid, and muriatic acid, there will, previous to crystallization, be no sulphate, nor muriate of potassa, but the acids will be in immediate combination with the potassa; each contributing to saturate it, in proportion to its affinity and quantity. If lime be added, it will merely share in the saturation; or if each of the acids be previously combined with a base,

potassa, for example, with sulphuric acid, and lime with muriatic, and the solutions of these salts be mixed, " the sum of the reciprocal forces of the acids and alkalies will be the same as before ; no muriate of potash or sulphate of lime will be formed; but there will be a combination of potash, of lime, of sulphuric and muriatic acids, which will have the same degree of saturation as before the mixture *. Or, in another example, given by Berthollet : " In a solution of sulphate of potash and muriate of soda, these two salts are not distinct, nor do they become so until some extraneous cause produces their separation ; sulphuric and muriatic acids, potash and soda are contained in the liquid."

On this rests the whole question ; for if this representation, that three or more substances form one combination, if no external force interfere, be just, then no doubt what have been named single and double elective attractions, must arise entirely from extraneous forces, and differences in the forces of affinity cannot even have a share in their production. But, on the other hand, if the opposite supposition can be admitted, that in mixtures of this kind binary combinations will be formed from the differences in the forces of their affinities, it will be impossible to avoid the conclusion, that the phenomena of complex affinity must in part arise from this difference, however much they may be modified by the circumstances which influence chemical attraction.

Now I am inclined to believe, that the latter hypothesis is, *à priori*, equally probable with the former, that there is no decisive evidence in support of the proposition which Berthollet has assumed, and nothing in the phenomena incompatible with the opposite opinion.

If all bodies had abstractly the same forces of affinity, it is obvious, that when three or more of them are placed together, nothing but extraneous forces could determine them to unite in binary compounds. But this supposition need not be consi-

* Researches, p. 104.

dered, since it is acknowledged, that independent of all external circumstances, their forces of affinity are extremely different. With this admission, then, let us consider what may be the result, if more than two substances, thus differing in the force of their affinity, are presented to each other; and let the example of single elective attraction, as it has been termed, or of three substances, two of which have attractions to the other, be first selected as the more simple.

Suppose two acids present with one base; it is admitted, that the forces of affinity of these acids to the base are very different. May not this, then, determine the manner and proportion in which they combine, or cause the acid which has the stronger affinity to combine, principally with the base, independent of any external force? If the compound thus formed have much tendency to cohesion, it will separate; but it does not follow that its cohesion, as the language of Berthollet implies, is the cause of its formation. This may be determined by the superior force of affinities in its principles; and it is only the separation of it from the sphere of action, that is produced by the cohesive power. It might even happen that the compound, the principles of which are united by the weakest attraction, has the greatest cohesion, and its separation will take place.

Or suppose a case of complex affinity, two acids and two bases being present, what will be the result? If no foreign force is exerted, says Berthollet, they will form one combination, both acids contributing to the saturation of both the bases; but if such a force interfere, it will give rise to binary combinations, which at the same time, from the exertion of that force, whether of cohesion or elasticity, will become apparent. Now this conclusion, it may perhaps be alleged, is not altogether clear; on the contrary, binary combinations, it may be supposed, may be determined by the different forces of affinity alone. Suppose one of the acids has a much stronger attraction to one of the bases than the other acid has; and suppose also that the latter acid has a much stronger attraction to the base to which the other acid has a weak affinity; will not the result of this be, that the acids will be divided be-

tween these bases in proportion to their affinities towards them? There may be some participation, but, from these different forces being exerted, it appears to follow, that the one acid will be combined principally with the one base, the other with the other, and thus give rise to binary combinations, or at least to combinations in which these two principles predominate, and in which, indeed, if there be certain proportions between the quantities and relative affinities, they alone will exist. It may be granted, that if no cohesion or elasticity is exerted, these binary compounds will not appear, for there is scarcely any property by which they can be detected. But it may still be maintained that they must be formed; and it is their appearance only, not their production, that is determined by the exertion of elasticity or cohesion. Hence is explained, as well on this hypothesis, as on that of Berthollet, the observation, which he regards as so favourable to his opinion,—that in complex affinity, the prevailing attraction has always been ascribed to those substances which form a compound that passes immediately to the solid or to the elastic form; for, in other cases, though the binary compounds might be formed, they would not be obtained insulated, and therefore the predominance of affinity would not be observed.

The only cause that occurs to me that it is possible to assign as preventing binary combinations, is the affinity which in the mixture of two compound salts the bases may reciprocally exert, and the affinity which the acids may also exert to each other, which may counteract the affinity of the one base to the one acid, and of the other to the other, and, added to what may be named the quiescent affinities of the acids to the bases, prevent the divellent ones from operating, and be balanced so as to produce one combination. But this, it is evident, must entirely depend on the forces of these affinities, and they in general appear weak. Admitting that they may be in some cases sufficiently powerful to prevent the binary combinations of the acids and bases, it is not to be assumed, nor indeed is it probable, that they will always be so; and where they are not, binary combinations must, according to the principles above stated, be

established from the different affinities of the acids to the bases.

Berthollet has stated, what he considers as a proof of his opinion, that "when two compound salts are mixed, the mutual decomposition of which would produce combinations of very different proportions, neither a redundance of acid or of base, which should necessarily result from such decomposition, can be observed. This has been very judiciously observed by Guyton. A change of base therefore does not take place *."

But in this argument it is taken for granted, that we know with accuracy the proportions of the constituent principles of these salts, which we certainly do not do; and the results observed by Guyton is a proof of this, not strictly a proof that there has been no exchange of base. Indeed the mutual saturation ought to remain the same, whether one combination or two binary ones be formed, because the sum of the reciprocal forces of the acids and bases remains the same, at least unless one of the salts has a strong tendency to form, either with an excess of acid or of base. The base which is combined with the weaker acid, will require a larger quantity of that acid for its saturation, proportioned to the weakness of the acid; and therefore, when it parts with that acid, and receives the stronger one, though there may be a smaller proportion of that stronger one, this will still produce the saturation, and prevent an excess of base, and, on the other hand, the base with which this latter was united, will require the larger quantity of the weaker acid for its saturation, and there can be neither an excess of acid or of base. If, therefore, calculations from the proportions of the ingredients of the salts mixed shew that there ought to be an excess of either, this only proves that the proportions have been inaccurately fixed.

The question can only be determined by the comparative probability of the respective assumptions *à priori*; for it is scarcely possible to prove either by experiment. Whether binary compounds are formed in a liquid or not, can be known

* Chemical Researches, p. 108.

only from their separation ; and when this happens, it must, on either hypothesis, be ascribed to the force of cohesion or elasticity ; so that we cannot say whether they had existed previous to the exertion of that force. And, on the other hand, if there is no separation, by what property or appearance shall we discover whether the principles exist in a mutual state of saturation forming one compound, or whether they form principally binary compounds, which remain in solution ?

In recurring, therefore, to the comparative probability of the hypotheses, it appears to me, that if four substances are brought together, a difference in the forces of their affinities may prevent an uniform combination, and by causing those which have the strongest affinity to combine principally together form binary compounds. Nor does this hypothesis exclude the influence of those circumstances, which Berthollet has so clearly proved have so great a share in the production of the phenomena of what have been named Single and Double Elective Attractions. They will either concur with them in the formation of the compounds, or counteract their exertion ; and the phenomena are not at all incompatible with the conclusion, that they arise from these forces, exerted under these reciprocal modifications. The commencement of the combinations will arise from the differences in the forces of affinity ; while if, on any of the binary combinations thus formed, cohesion or any other force producing its separation be exerted, this will favour the completion of the combination, by withdrawing the principles from the reciprocal action of the others.

If, on the other hand, we consider more closely Berthollet's theory of complex affinity, that binary combinations arise solely from the exertion of extraneous forces, some difficulties may perhaps be urged against it, which the admission of the influence of the different forces of affinity will even remove.

Thus, on the assumption, that when four substances are presented to each other, they would form a simultaneous combination, were not some external force, that of cohesion for example, exerted, it is difficult to discover how it can operate in giving rise to binary combinations. This operation may be con-

ceived to be, either on the *principles* of the combination causing those two which have the greatest tendency to cohesion to combine together, or on the *compound* itself producing its separation, and thus removing the resistance which might be opposed to the progress of the combination, if it remained within the sphere of action. It is not very clear, from the language of Berthollet, under which of these views he regards the influence of cohesion. But I believe I may affirm, that either of them is inadequate to the explanation of the phenomena of complex affinity, on the assumptions that the relative forces of affinity have no share whatever in giving rise to binary combination, that the tendency always is to form a single combination with affinities mutually balanced, and that binary compounds are formed entirely by the exertion of an external force.

Thus, to consider the influence of cohesion under the first point of view,—that of four principles presented to each other in a common fluid, the two which have the strongest tendency to cohesion, will, from this circumstance, be those which will be combined, we do not perceive, since all the substances are in a state of solution, how the cohesion alone can combine two of them. The immediate result of their attractions, it is said, is to form one combination. From the density resulting from that combination, such an addition might be made to the force of cohesion as to cause *it* to separate; but we perceive no reason why this should give rise to the binary combination; while, if that combination were determined by the superior force of affinity, it is easy to perceive that the separation of the compound might be produced in consequence of the accrued condensation. Nor in appealing to fact do we find that in such mixtures the principles which are combined together are always those, which, in their insulated state, have the greatest tendency to cohesion. They sometimes, no doubt, are so, as for example in adding to muriate of barytes sulphate of soda, where the two principles, which, in their insulated state, have undoubtedly the greatest tendency to cohesion, the sulphuric acid and the barytes are those which combine. But, in many other cases, this cannot be observed. Thus, in mixing solutions of nitrate

of silver and muriate of soda, could it be inferred, on this principle, that the muriatic acid and the oxide of silver should be those which are combined? The oxide of silver is of the four substances no doubt the one which is least soluble in the fluid which is the medium of action, or which has, under the circumstances which are present, the greatest tendency to cohesion; and, therefore, on the hypothesis, it might be predicted that it would enter into the composition of the compound which is precipitated; but of the two acids we should have no reason to suppose, independent of the influence of the force of affinity, that the muriatic would be the one with which it would combine, but precisely the reverse; for, of these acids, the nitric is the one which has the greatest tendency to cohesion, as is shewn by it being easily condensed, and being even susceptible of congelation from cold, which the muriatic is not. Though the compound, therefore, of muriatic acid and oxide of silver has more tendency to cohesion than that of nitric acid and oxide of silver, it cannot be said, that previous to the combination, the sum of the forces of cohesion of the two former is superior to that of the two latter.

This leads to the consideration of the other point of view, under which the influence of cohesion on the results of complex affinity may be regarded,—that of four principles, the two which will be combined (leaving of course the other two also in binary combination) are those which form an insoluble compound. This no doubt accords much better with facts. But, in adopting this view, we at once fall into the absurdity of assigning a property of a compound as the cause of the formation of that compound. If the result, independent of foreign forces, is to form an individual combination, it is perfectly obvious that this cannot be disturbed by any force which would appear, if that combination were subverted, and binary compounds formed. There must be some cause to first produce these compounds, before any influence can arise from any property, of which, where they are formed, they are possessed. It is not possible, by any additional illustration, to place this in a clearer light.

From the preceding observations I would consider it as very

doubtful, whether Berthollet has not extended too far the principle on which his theory of complex affinity is established. Although cohesion and other external forces may influence the results, it may well be doubted if they are the sole cause of them, as that theory assumes. It is admitted, that there are differences in the abstract forces of affinity, as exerted by different substances. When three or four substances are mixed together, such differences must, we should imagine, determine them to form binary combinations, and prevent a simultaneous combination with mutual saturation; and although cohesion or elasticity may co-operate with these affinities, or in other cases may counteract them, still the effects which result are not to be ascribed entirely to their operation, but in part to the differences in the forces of affinity which are allowed to exist.

The determination of the question would be of considerable importance, not only in a theoretical point of view, but also in practical chemistry; for, if we exclude causes which have a share in the production of these phenomena, important errors may be committed: if we ascribe entirely to cohesion or elasticity what is partly due to these powers, modified by respective forces of affinity, we are led aside from the just view of the causes of the phenomena: we may assume false data, by considering as simple what is in reality complicated; and we may neglect what in many cases are truly the productive forces, and rely upon others which are of less importance.

c. *(p.* 135.*)*—From the preceding discussion it will be obvious, that no question can be more interesting, nor is there one, the solution of which would afford more important applications, than that which relates to the absolute forces of affinity possessed by different bodies; at the same time there is none, the precise solution of which is more difficult. In the text I have given an account of the methods that had formerly been proposed; mentioned their deficiency; and added the general principle, the results of Mr Kirwan's labours, from which may, with most probability, be deduced the measure

of the forces of affinity. On this subject I have still to add a few details.

Among the chemical properties of bodies, there is frequently one which is predominant, and which gives to the substances possessing it a common and well-marked character. Of these characteristic properties some are opposed to each other; one class of substances possessing one, another possessing precisely the opposite. Thus the characteristic properties of the class of acids are precisely the reverse of those of the class of alkalies. In the combination of two bodies belonging to these opposite classes, the adverse properties neutralize each other with reciprocal force, and at a certain stage they disappear, or a compound is formed in which neither predominates. This stage is termed the point of neutralization or saturation, and the two bodies combined in this proportion are said to have neutralized each other, or to be mutually saturated.

Now, this power of producing neutralization may be considered as arising from the force of affinity which the body exerts, and may therefore be regarded as a measure of that force. This view seems to have occurred to Mr Kirwan; though in order to reconcile the principle with the established order of elective attractions, he adopted it only partially. In making experiments on the composition of the neutral salts, he discovered that a relation subsisted between the quantities of these substances necessary to produce reciprocal saturation, and their apparent forces of affinity; and in prosecuting his experiments he was led to establish the following principles: — First, That the quantity of real acid necessary to saturate a given weight of each base, is inversely as the affinity of the base to the acid; and, secondly, That the quantity of each base requisite to saturate a given quantity of each acid, is directly as the affinity of the acid to the base. The quantities of the different bases requisite to saturate equal quantities of the three principal acids, according to these experiments, are given in the following table *.

* Philosophical Transactions, vol. lxxiii. p. 38.

100 Grains of	Potash.	Soda.	Lime.	Amm.	Magn.	Argil.
Sulphuric Acid	215	165	110	90	80	75
Nitrous Acid	215	165	96	87	75	65
Muriatic Acid	215	158	89	79	71	55

In this table, the gradations in the quantities necessary for saturation, appear to correspond with the differences supposed to exist among these bodies in the forces of their attractions; and Mr Kirwan concluded, that these numbers might be regarded as expressing the relative forces of these affinities. Thus the affinity of potassa to sulphuric acid, being 215, that of soda to the same acid may be considered as 165, and that of lime 110. He showed also that they correspond with actual decompositions. Thus, on mixing nitrate of lime and sulphate of potassa, a double decomposition ensues; and that this would be the case, might be predicted from Mr Kirwan's table, which shows the divellent affinities to be superior to the quiescent; the former, those of nitric acid to potassa, and of sulphuric acid to lime, being $215 + 110 = 325$; while the latter, those of sulphuric acid to potassa, and nitric acid to lime, are only $215 + 96 = 311$.

But if we proceed to examine the numbers given in this table by this test, we do not always find this correspondence; on the contrary, decompositions happen on mixing compound salts together, which ought not to take place were the numbers just, of which Guyton, under the article *Affinité*, Encyclopedie Méthodique, gave several examples.

This, however, does not prove the fallacy of the principle on which the method is founded, since such deviations might arise from errors in the estimation of the proportions of the ingredients of the compound salts, or of the quantities of acid and base requisite for mutual saturation, and there can now be no doubt of the existence of such errors. The numbers were deduced from experiments, which were not only liable to important sources of fallacy, but which were farther vitiated by having been combined with assumptions which Mr Kirwan had

since acknowledged to be inaccurate. Resuming his labours, he accordingly gave corrected and more extensive tables, in which the numbers are entirely different, first in the fourth volume of the Transactions of the Irish Academy, and afterwards, with some additional corrections, in the seventh volume of the same work. The latter tables I shall transcribe.

TABLE I*.

100 Parts of	Potash.	Soda.	Ammonia.	Barytes.	Strontites.	Lime.	Magnesia.
Sulphuric Acid	121.48	78.32	26.05	200.	138.	70.	57.92
Nitrous Acid	117.7	73.43	40.35	178.12	116.86	55.7	47.64
Muriatic Acid	177.6	136.2	58.48	314.46	216.21	118.3	89.8
Carbonic Acid	95.1	149.6	——	354.5	231.+	122.	50.

TABLE II.

100 Parts of	Sulphuric Acid.	Nitrous Acid.	Muriatic Acid.	Carbonic Acid.
Potash	82.48	84.96	56.3	105. almost.
Soda	127.68	135.71	73.41	66.8
Ammonia	383.8	247.82	171.	Variable.
Barytes	50.	56.	31.8	282.
Strontites	72.41	85.56	46.	43.2
Lime	143.	179.5	84.488	81.81
Magnesia	172.64	210.	111.35	200.—Fourcroy.
Argil	150.9	——	——	335.—nearly, Bergm.

* Transactions of the Irish Academy, vol. vii. p. 294.

Though the proportions given in these tables probably approach much more to the real proportions than those given in the preceding one, it may still be doubted whether they are perfectly correct. Some just observations on the errors attached to the methods Mr Kirwan employed in these investigations are made by Berthollet*; and if their according with the order of decompositions were a proof of their accuracy, he has given some examples which do not stand this proof. It is known, for example, that on mixing muriate of barytes with sulphate of potassa, there is an exchange of base; yet, according to the preceding table, the quiescent affinities are superior to the divellent, the former being $314.46 + 121.48 = 435.94$, while the latter are only $177.6 + 200 = 377.6$.

Guyton had on this subject proposed a mode of verification extremely simple, and which appears to be just. He observes, that when two neutral salts in solution are mixed together, and a double decomposition ensues, the result of the mixture must be, either that it remains neutral, or that it has an excess either of acid or of base. If it be found from the tables which have been given of the proportions of salts, what quantities of acid and of base are contained in each of the salts mixed in such an experiment, and what quantities of acid and of base are contained in each of the new salts that are formed, on a double decomposition ensuing on their mixture, it is easy to discover whether in the original salts there was more or less of each acid than what would be requisite to saturate each of the bases in the new salts, and of course whether the compounds should be neutral, or should have an excess of acid or base. If, on making the experiment, the result do not accord with the result obtained by the calculation, it follows, that the estimate in the proportions of one or both of the salts must be incorrect.

Guyton, proceeding on this principle, has made some experiments with a view of ascertaining the accuracy of the tables of the composition of neutral salts given both by Bergman and

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* Chemical Statics, vol. i. p. 78.

Mr Kirwan. Thus, referring to Mr Kirwan's table, published 1791 *, the following are the proportions of acid and base requisite for mutual saturation in the following salts.

Sulphate of magnesia,	100 of acid,	56.6 of magnesia.
Sulphate of soda,	100 of acid,	70 of soda.
Muriate of soda,	100 of acid,	68.5 of soda.
Muriate of magnesia,	100 of acid,	46.3 of magnesia.

Now, when solutions of muriate of magnesia and sulphate of soda are mixed together, there is an exchange of base. Guyton, on making the experiment, found also that the mixture remained perfectly neutral. Let us apply the calculation then to discover, if, from the preceding numbers, regarding them as the proportions of the constituent parts of these salts, this ought to have been the case.

The muriate of magnesia, according to the table referred to, exclusive of water, consists of 100 of acid, and 46.3 of magnesia. This quantity of magnesia, in combining with sulphuric acid, will require only 81.802 of that acid; for sulphate of magnesia, according to the table, consists of 56.6 of magnesia and 100 of acid, and 46.3 is to 81.802 as 56.6 is to 100. But if this new combination abstract only 81.802 of sulphuric acid, no more than 57.261 of soda will be set at liberty, this being in the relation of 100 of acid to 70 of base in the sulphate of soda. Now it appears from the table, that 68.5 of soda are necessary to saturate 100 of muriatic acid; but as there is only set at liberty a quantity of soda capable of neutralizing 83.392 parts, there must remain 16.408 unsaturated, which ought to communicate acidity to the mixture. This however remains neutral, and therefore the proportions in some, or perhaps in all of these salts, must be wrong. Guyton finds the same result in another example from Mr Kirwan's table, that of the decomposition of sulphate of potassa and nitrate of lime†. The

* Transactions of the Irish Academy, vol. iv. p. 68.

† Mémoires de l'Institut National, tom. ii. p. 333.

numbers denoting the proportions of the salts, are in both cases different in Mr Kirwan's last table; but still, on applying to it this mode of verification, similar general results, with deviations even greater, will be obtained, as Berthollet has shewn by several examples *.

The fact on which this mode of verification, so happily conceived by Guyton, rests, that a change in the state of saturation does not happen on mixing solutions of compound salts, appears to have been first attended to by Richter, of whose observations a short account is given by Fischer, in a note at the end of Berthollet's treatise †. Berthollet himself has subjected it to experiment, and has found it to hold true, where salts are not formed having a tendency to exist with an excess of acid or of base; and he has also applied it to various salts, the proportions of which are given in Mr Kirwan's table, and with results similar to those stated by Guyton ‡. No tables of this kind can be relied on, which are not verified by this method, so that the proportions assigned correspond with the results of such experiments.

The principle, however, which results from these facts, is highly important, and, as is observed by Berthollet, must abridge the labour of ascertaining the proportions of such compounds. The principle is, that there exists an uniform relation of quantity between the acids in their combinations with the different bases in producing saturation. The same base, in its relations to the different acids, (and the proposition applies equally to the acids in their relations to the bases), will require, if the expression may be allowed, the same expenditure of acid power for its saturation; so that if it require a large quantity of an acid having a weak affinity, it will require for the same effect a proportional small quantity of an acid having a stronger affinity. Hence, if two neutral salts are mixed together, the base in each must have combined in it the same

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* Chemical Statics, vol. i. p. 86.

† Chemical Statics, vol. i. p. 400. ‡ Ibid. p. 86.

quantity of acid power; and therefore, after the mixture, the state of saturation must be as before. If, for example, sulphuric acid be combined with potassa, and muriatic acid with lime, each to saturation, forming two neutral salts; on mixing them, if an exchange of bases happen, the quantity of potassa, which was saturated by a certain quantity of sulphuric acid, will require such a quantity precisely of muriatic acid that the lime left by that acid will also be saturated exactly by the sulphuric acid which the sulphate of potassa had yielded; at least this will be the case, unless, where triple salts are formed, or where, from the influence of external circumstances, one of the compounds forms with an excess of acid or base. Excluding these circumstances, Berthollet remarks, that to determine the composition of neutral salts, "nothing more is required but to determine with care the proportions of an acid with the different alkaline bases; it will then be sufficient to ascertain the proportions of a single combination of each of the other acids with an alkaline base, taking that which is the most convenient for experiment, and an easy calculation will give the proportions of all the others *."

Besides the table of Mr Kirwan, which at least presents approximations to the real proportions, I may insert in this place one calculated by Fischer from Richter's experiments, which, although the accuracy of the numbers may be regarded as still more doubtful, is of value from the simplicity of its construction, and as at once pointing out the powers of saturation in the different acids and bases. This table consists of two columns, one composed of the acids, the other of the alkalies and earths, with numbers annexed to each. It is thus to be understood: If an article in one of the columns be taken, suppose potassa in the first to which the number 1605 belongs, the numbers affixed to the names of the substances in the other column will show how much of each of these is requisite to saturate these 1605 parts of potassa: they will require, for example, 427 of fluoric acid, 577 of carbonic acid, &c. If,

* Chemical Statics, vol. i. p. 89.

again, we take an article of the second column, the first will indicate, in the same manner, how much earth or alkali will be required to neutralize it *.

Bases.		Acids.	
Argil,	525	Fluoric,	427
Magnesia,	615	Carbonic,	577
Ammonia,	672	Sebacic,	706
Lime,	793	Muriatic,	712
Soda,	859	Oxalic,	755
Strontites,	1329	Phosphoric,	979
Potassa,	1605	Formic,	988
Barytes,	2222	Sulphuric,	1000
		Succinic,	1209
		Nitric,	1405
		Acetic,	1480
		Citric,	1683
		Tartareous,	1694

It is easy by calculation to reduce these numbers in any example to 100 parts. From some observations formerly made by Mr Kirwan on Richter's experiments †, there appears however to be much reason to doubt of the correctness of the numbers that have been deduced from them.

In these tables, either Kirwan's or Richter's, it will be obvious, that the correspondence between the quantities of the respective substances necessary for saturation, and the common orders of their affinities, does not exist; and if the numbers be applied to denote the strengths of affinity, they will often appear at variance with the results of experiment. This occurred to Mr Kirwan, and, in consequence, he appeared to have relinquished the hope of attaining by this method the solution of the original problem.

The views of Berthollet, however, throw more light on this subject; for they shew that were the numbers much more remote than they are from the usual order of elective attrac-

* Chemical Statics, p. 402.

† Transactions of the Irish Academy, vol. vii. p. 286.

tions, this is no proof that they may not express the real forces of affinity. In attempting, indeed, to solve this problem, the hypothesis always hitherto proceeded on has been, that affinity is an invariable force, not influenced by adventitious circumstances, and that the order of attractions, drawn from the usual decompositions, is the real order of the forces of affinity. Hence the attempt has been always made to approach to this order as nearly as possible, and the attainment of this has been regarded as the test of the justness of the solution. Chemists must now be convinced that this is a mistake. The common order of elective attractions,—that order, for example, which considers the affinities of sulphuric as superior to those of nitric acid, and those of nitric to those of muriatic, or the affinities of potassa as more powerful than those of soda, and those of soda than those of ammonia,—has been deduced from a series of decompositions, which arise not merely from different strengths of affinity, but from these materially modified by various external forces. Hence attractions, which, from the influence of these forces, appear in experiment strong, may be actually weak; and others, which, from the operation of the same causes, appear feeble, may be comparatively strong; nor, if the real order of the forces of affinity should be deduced from any principle, is there any reason to expect that it should correspond with the common order of elective attractions.

Berthollet has therefore adopted the broad principle, which we have already stated,—that the power of saturating opposing properties, is the result of the force of affinity; and this leads him to arrange the forces of chemical agents in nearly an inverse order of that which appears in the usual tables of elective attractions. As the reciprocal saturation of substances combined together, is the immediate effect of their affinity, independent of foreign circumstances, it may be regarded as the measure of that affinity; and as unequal quantities of different agents, of acids, for example, are requisite to saturate any common base, the forces of their affinity, considering them always as acting in equal quantities, must be different, and may be estimated from the quantities requisite to produce saturation, or in the sense in which Berthollet employs the term, neutralization. The

principle, therefore, assumed, is, that the affinities of the different acids to the same base is in the inverse ratio of the quantity of each of them which is necessary to saturate or neutralize an equal quantity of that base, or, the less of an acid requisite to produce the saturation, the more energetic is its affinity, or the greater is its force. This is the principle of Mr Kirwan; but he, finding that were it also applied to the affinities of the bases to the acids, it would be totally inconsistent with the observed order of elective attractions, and with the results of experiments, reversed it as applied to these bases; and although he thus established a correspondence between the order deduced from the principle, and that of the usual tables of affinities, he subjected his hypothesis to the unanswerable objection, that it involved a contradiction; that, on one hand, it supposed a greater affinity to require a less quantity of a substance to produce saturation, and that, on the other, it required a greater quantity.

Berthollet, disregarding the established order of affinities, applies the same principle to all cases, and therefore the axiom which has now been delivered with regard to the affinities of the acids to the bases with which they combine, equally holds with regard to the affinities of these bases to the acids; or the base, which in the smallest quantity saturates an acid, is that which possesses the greatest affinity. The principle, in short, as extended to all chemical agents, is, that the affinity of any substance to another is more powerful, as a given weight of it can saturate a greater quantity of that other.

Admitting this principle, and taking the corrected table of Kirwan as indicating the quantities of the acids and of their bases necessary for saturation, it will follow, as will be evident on inspection of that table, that the muriatic acid, as it saturates the largest quantities of the different bases, is that which exerts the most powerful affinities; next to it is the sulphuric, and then the nitric acid. The estimate of the affinities of the carbonic acid cannot be so much depended on. They deviate considerably from the order observed by the others, and there are peculiar difficulties in ascertaining with accuracy the proportions of the carbonates. If we likewise take into consi-

deration the most accurate experiments that have been made with the other acids, it will be found as Berthollet has remarked *, that the phosphoric acid precedes the muriatic, and the fluoric the phosphoric, 1000 parts of phosphoric saturating, according to Vauquelin, 1440 of lime, and 1000 of fluoric saturating, according to Richter, 1882, while 1000 of muriatic, from Kirwan's table, appear to be capable of saturating only 1183. This gives us therefore the strength of affinity in these acids in the following order: fluoric, phosphoric, muriatic, sulphuric, nitric.

With regard to the different bases with which the acids combine, if the principle be just, the order of their real affinities is nearly inversely that of their apparent forces, such as they are estimated from the phenomena of decompositions. From Kirwan's tables, it appears, that the affinity of ammonia must exceed that of the others, as a smaller quantity of it saturates given quantities of the acids; next to it are magnesia and lime, then soda and potassa, and, lastly, strontites and barytes.

It is sufficiently evident, that these arrangements of the forces of affinities deviate widely from the received order. To connect the one with the other, it is necessary, says Berthollet, to seek in the habitudes of the substances which combine, and in the conditions in which they may be found, the explanation of the facts which lead to conclusions so opposite. It is to the force of cohesion principally, the effects of which have been confounded with those of affinity, that the difference is to be ascribed, and partly also to elasticity, which likewise operates as a modifying power; but whatever may be the opinion retained with regard to elective affinity, it is impossible to deny that a strict relation subsists between its force, and the power which substances have of producing reciprocal saturation.

Admitting, however, the truth of the preceding reasoning, much uncertainty must still remain as to the expression of the forces of affinity, from the difficulty of ascertaining the real

* Chemical Statics, vol. i. p. 92.

proportions of bodies requisite for saturation. If the difficulties are such, too, with regard to substances, which we can so easily subject to experiments that might be deemed accurate, as the acids and alkalies, what labour would be requisite to extend the same researches to many other chemical agents?

It must also be evident, that we can no longer look for those practical advantages from the solution of the problem of estimating the forces of affinity, which were formerly expected from it. While affinity was regarded as an uniform force, it was imagined, that were its intensities discovered, we might be able to predict the results of its exertion independent of experiment. But it is obvious, that were we even in possession of the scale of affinities, we could not foretel, in any given case, what would be their results, since they are modified by external circumstances, which totally alter their relative forces. We probably could not subject to calculation the complicated effects of cohesion, elasticity, quantity, and other modifying powers; and we should therefore be altogether unable to foresee the effective forces that would be exerted.

Note B.

The only part of the chemical history of caloric which requires a more ample discussion than could have been introduced with propriety into the text, is that which relates to its distribution in bodies, and the state in which it exists. Does it exist in them merely as the cause of temperature; or besides this, is it in any case in a state of more intimate combination, or united by a more energetic affinity, so as to be deprived of its characteristic properties? On this question, regarding free and combined caloric, the opinions of chemists are still undetermined: the subject has at the same time not often received a full discussion; and mistakes with regard to it are by no

means unfrequent in the writings even of those who are otherwise well informed in chemical science.

There are two points of view under which the chemical combination of caloric has been considered, very different from each other, and which, therefore, it is necessary to consider apart. The absorption and apparent loss of properties of caloric in fluidity and vaporisation, have been considered as owing to an intimate combination into which it enters with the body fused or evaporated, and as perfectly analogous to other chemical combinations; while other philosophers, without expressly maintaining this opinion, have supposed that caloric may enter into a more intimate union with bodies than that in which it exists in them when it produces expansion and its other effects, and that in all bodies a portion of it exists in this combined state.

1st, It has been conceived, that in liquefaction and vaporisation the portion of caloric which becomes latent, is chemically combined with the body which has suffered the change of form, and that this change, as well as the latent state of the caloric, are owing to this combination. I have already observed (p. 407.), that Dr Black inclined to this opinion, and that it has been maintained in more decided language by De Luc*, and by a number of the French chemists. It is thus stated by Seguin, in his review of the doctrines of heat connected with this subject: "Until the moment of liquefaction, the caloric in a body is merely interposed; but during this change, there is a new combination of it, resulting from a superior affinity. The moleculæ of a solid unite with a certain quantity of caloric to form a liquid. This caloric is absolutely necessary to the form of this new body. This liquid has interstices, which will be filled by the caloric, which before liquefaction was interposed between the particles of the solid, in such a manner, that the distance between the particles of the new compound will be very nearly equal to that which existed between those of the

* Idées sur la Meteorologie, tom. i. p. 179.

solid from which it has been produced. We may therefore consider, as existing in every liquid, two portions of caloric, entirely distinct; one which acts on the thermometer, and determines the temperature; another which has no such effect *."

I have likewise stated in the text, that Dr Irvine regarded these changes of form as produced by the operation of sensible caloric alone; and the absorption of caloric during liquefaction and vaporisation, together with its latent state in the fluid and vapour, he considered merely as the consequences of the augmentation of capacity which he discovered to attend these changes of form.

It is obvious, that the change of form in these cases, and the evolution or absorption of caloric being, at least to our observation, simultaneous, we have no direct means of discovering which precedes the other. We must therefore seek to determine the merits of these opinions on other grounds.

If we regard them merely as hypotheses, we must at once prefer that of Irvine, as more simple and philosophical, and more analogous to the relations of caloric to matter. We have seen, that the capacities of bodies are intimately connected with their mechanical state, with the arrangement of their particles, so much so as to justify the inference, that when the arrangement is altered, the capacity will be changed. We must also be satisfied *à priori*, that at some stage in the scale of temperature, the changes of fluidity and vaporisation must take place from the operation of sensible caloric. In such changes there is an alteration in the mechanical state of the body; and nothing can be more probable, *à priori*, than that the very change of capacity which is supposed in the theory should be the consequence. We know nothing of the properties of caloric in an insulated state, but merely the effects of it on matter; and no reason can be stated in support of the proposition, that its effects on bodies of different kinds, or in different states, should be the same. If a solid body have a certain relation to caloric; suffer from it,

* Annales, tom. iii. p. 193.

for example, a certain degree of expansion; conduct it, after a certain ratio; or require a certain quantity of it to produce a given temperature; if the constitution of that body is changed, though it be by the action of caloric itself, if, for example, it is converted to the fluid or aëriform state; it is evident, that we have no reason to expect that its relations to caloric should be the same as they were in the solid state. We find in reality that they are totally changed; that the body now suffers a different degree of expansion from this power from what it did formerly; and that its conducting power with regard to it, is no longer the same. We may presume, therefore, that a similar alteration must take place with regard to its other relations to caloric; that it must require a different quantity to produce a certain change of temperature, or, in other words, must acquire a different capacity.

Nothing also can be more obvious, than that if such a change do happen, the augmentation of temperature will observe a different law from what it did, while the body was in its former state. If by fusion, or vaporisation, the capacity of a body be enlarged, either its temperature must fall, or a quantity of caloric must be absorbed, by which no augmentation of temperature will be produced. The first cannot happen, for in this case the temperature of the body falling below its fusing or evaporating point, the change of form cannot proceed; the second event, therefore, must be that which will occur, or, if by constantly applying caloric, we raise and preserve the temperature sufficiently high to cause the change of form to proceed, then if this change of form be accompanied by an increase of capacity, a quantity of the caloric applied must be constantly absorbed, and must become latent, or occasion no increase of temperature. The phenomena, therefore, attending fusion and vaporisation, are precisely those which should occur, if, according to Dr Irvine's hypothesis, these changes are accompanied by an enlargement of capacity.

The opinion of Dr Irvine is thus at once probable *à priori*, and fully adequate to the explanation of the phenomena.

The opposite opinion, considering it also as an hypothesis, has no such probability. We see no cause, for example, why, for a great extent of the thermometrical scale, bodies should receive caloric without entering with it into any intimate combination; why, when the temperature is raised to a certain point in each body, this combination should suddenly take place; and why, after another interval in the thermometrical scale, it should be renewed; why, for example, water at 32°, and under the common atmospheric pressure at 212°, and at these points only, should contract an intimate union with caloric.

Nor are the phenomena attending these changes of form strictly analogous to those of chemical combination. Although, on a superficial glance, a portion of caloric appears to lose its properties; and this may be supposed to render probable the proposition, that it has entered into an intimate combination, (and it has generally been regarded as a proof of that proposition,) a more enlarged view of the subject shows us, that we really cannot affirm that any portion of the caloric has sustained this loss of its characteristic qualities. The apparent loss is owing rather to the body having acquired a new relation to this power, in consequence of which it requires a larger quantity to produce a given state of temperature. The properties of caloric are, to produce expansion, fluidity and vaporisation, or, in general, that condition of bodies denominated temperature; but it is no property of caloric, that an equal quantity of it shall produce in all bodies the same temperature. Precisely the reverse is true. If, therefore, when a body is fused, or is converted into a vapour or gas, a portion of caloric is absorbed, which has no effect in raising the temperature of that fluid or vapour, it is a mistake, or at least an unsupported assertion, to say, that here a portion of caloric has lost its properties: it is rather the body in which it resides that is changed, its mechanical constitution is altered, and, with regard at least to its relations to caloric, it has become a new substance. Conformable, therefore, to the general law which caloric observes in its distribution, it must require a different quantity to produce in it

a given temperature. Nor is there more reason for saying, that the properties of the excess of caloric, which water has above ice at 32°, are lost, than for affirming the same thing with regard to the excess of caloric which water contains above quicksilver at the same temperature. The latent state of a portion of caloric, in different forms of the same body, is precisely the same with the latent state of that portion of caloric which one body contains more than another, their temperatures being equal. The latter cannot be ascribed to chemical combination, as I shall have immediately to show, and the former cannot, with more reason, be referred to that cause.

It is this apparent loss of properties that has always given rise to the supposition, that caloric must, in these changes of form, enter into a state of more intimate combination. But this is entirely a mistake. What is understood by the phrase, Capacity for Caloric? Is it not the expression of the general fact, that a body requires a certain quantity of caloric to produce in it a given temperature? The truth of such a fact, or the existence of such a property, is undeniable. What must happen if the capacity of a body is enlarged? It must require more caloric to produce that temperature; and hence, to preserve it at the temperature at which it exists when the enlargement of capacity happens, a quantity of caloric must be absorbed. Yet although this caloric does not raise the temperature of the body, it is not deprived of its properties; it goes with the rest of the caloric contained in the body to preserve the existing temperature, and, were it deprived of its properties, or did it enter into any intimate combination, the temperature of the substance which receives it would, in consequence of its augmented capacity, actually sink, unless it received some other portion of caloric which retained its properties. These are propositions which must be admitted if they are understood; and they shew at once, that the circumstance of the caloric absorbed during liquefaction and vaporisation, not producing any rise of temperature, or not being discoverable by the thermometer, is no proof whatever that that caloric has changed its mode of existence, or entered into any peculiar combination, since this would equally happen from an

augmentation of capacity. The one cause may indeed *hypothetically* be assigned as well as the other, but, if the augmentation of capacity be *experimentally* proved, it must be assigned as the real cause, and the other, being purely hypothetical, must be excluded.

In other points of view, there is not the least similarity between the absorption of caloric in liquefaction and vaporisation, and the usual cases of chemical combination. Although the properties of the caloric are supposed to be completely lost, none of the chemical qualities of the body combining with it, and producing this energetic effect, are in the slightest degree changed. Since every body is capable of being fused, and converted into vapour, we must suppose that all bodies are capable of combining intimately with two proportions of caloric, and with two only; a singular law, not observed in the combinations of other agents. We find too, that every vapour may be rendered fluid, and every fluid solid, by communication with a body at a lower temperature, though the caloric thus abstracted from the vapour or fluid does not enter into combination with the substance abstracting it, but serves merely to elevate its temperature; a fact sufficient to shew, that, in the substance from which it was abstracted, it was not more intimately combined than in the one to which it is communicated. Nay, there can be no doubt, that a fluid might be frozen *in vacuo*, or might give out the caloric supposed to be chemically combined with it, without that caloric being attracted by any other matter. These facts are sufficient to shew, that what is named Latent Caloric is not retained by any attraction different in kind or degree from caloric of temperature.

So far regarding these explanations as hypothetical, it must appear that Dr Irvine's is more probable than the other, and more consonant to the phenomena; and to establish it as a just theory or interpretation of a law of nature, nothing is requisite but that its principle,—that a change of capacity accompanies the change of form, be proved by experiment.

This subject, I have remarked in the text, engaged the attention of Dr Irvine for a considerable length of time, and led

him to undertake many experiments. The general nature of the experiment has been described, and is perfectly unexceptionable; the capacity of the same body being ascertained first in its solid, and secondly in its fluid state, without the body suffering any change of form in the progress of the experiment. Dr Irvine "found the capacities of some suitable bodies, as river-sand, or iron-filings, and compared them with that of water in the usual manner. This being done, he used the same body to examine the capacity of pounded ice formed from distilled water, or of snow. The temperature of the room and vessel was, in his experiments, always either 32 or below it; most commonly considerably under 32°. He then took a known weight of snow or ice of a known temperature, in a vessel of which the capacity was determined by experiment. Upon this he poured a certain quantity of river-sand washed, or iron-filings of a certain temperature, with as much rapidity as possible. The new temperature was observed after stirring, and allowance was made for the heat gained or lost: the temperature of the mixture was frequently 19°, 20°, 25°, 16°, &c. So that in a room where the air was below the freezing point, the accuracy of the result could not be affected by the formation of any water; still there are many sources of inaccuracy remaining. But in Dr Irvine's hands, the capacity of ice always turned out to be less than that of water. In all his experiments, which were very numerous, and repeated with care for many succeeding years, he arrived at results approximating to each other, and concluded, to use his own words, that from the mean of all his trials, the capacity or relative heat of water to that of ice is not in a ratio greater than 5 to 4 or 10 to 8. In like manner, Dr Irvine extended his theory to all other bodies whatever, and in some cases determined, and in all inferred, that it is a general law of nature that the capacity of all solids for heat is increased by fusion, and that of all fluids by vaporisation *."

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* Chemical Essays, p. 55.

It may be said, that although it be proved that when fluidity and vaporisation take place, there is an augmentation of capacity, still it is not proved that the augmentation is proportional to the quantity of caloric absorbed; and that, therefore, part of that caloric may be absorbed from some other cause, and exist in some other state. But how is this to be determined? It is impossible to establish the fact on either side; for to do so, it would be necessary to know the absolute caloric of bodies, and this from a mode of experiment independent of changes of capacity from alteration of form. Now this has not been ascertained with such accuracy as to admit of any certain conclusion. If it could be proved, or even rendered probable by a single analogy, or by any fact, that the augmentation of capacity is not proportional to the absorption of caloric, the theory of Irvine would require to be corrected. But when this is not proved, and when the supposition is not necessary to account for the phenomena, why should it be made? An augmentation of capacity is proved to take place; it must give rise to an absorption of caloric; and it may be sufficient to account for the whole quantity absorbed. It is surely inconclusive, and a mode of reasoning discarded from physical investigation to say, that perhaps the augmentation may not be proportional, and that therefore a portion of caloric may exist in the fluid or air in some other state. Such possibilities might be urged in support of every antiquated notion, and against every established theory in chemistry. "Since the existence of a cause," says Crawford, "sufficient to account for the appearances, has been established by experiment, it seems inconsistent with the simplicity of the operations of nature to suppose, that other causes, for the existence of which there is no experimental proof, concur in the production of the same effects; for nature does nothing in vain; *et frustra fit per plura quod fieri potest per pauciora**."

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* Newtoni Princip. lib. iii. p. 357.

It is incumbent on me to take notice of an objection, the only one of any apparent force, that has been urged against Dr Irvine's theory. It was stated by Dr Black, and has often been proposed as unanswerable. It is, that supposing the absorption of caloric, and the latent state of the quantity absorbed, to arise from an increase of capacity in the fluid or vapour, no cause is assigned for the change of form. "The alleged fact of disparity between the capacity of ice and water for heat," says Dr Black, "may indeed be supposed to account for the thermometrical phenomena just now recited; but the principal fact or phenomenon is not accounted for by it, I mean the change of the solid into the fluid. Solidity, we all know, depends on cohesive attraction; but on what cause does fluidity depend? Will it be said to depend on the absence or cessation of cohesive attraction? I cannot imagine how cohesive attraction can entirely cease, or be suspended, or, if this should happen, how it should easily be again restored: Nay we have evident proof, from the round form of the drops of liquids, that it is not in them entirely suspended, but only weakened to such a great degree, that the solid hard body is become a liquid. Now this is such a violent change, that I cannot help thinking it must depend on some powerful cause. It may be said, perhaps, that no other cause is necessary but the increase of sensible heat above a certain degree, together with some singularity in the nature of cohesive attraction; such as that this attraction, though very strong at certain small and imperceptible distances, becomes suddenly very weak, when we increase, beyond a certain limit, the distance of the particles of matter from one another, and this increase of distance is produced by sensible heat. If this were true, the increase and diminution of distance by the action of sensible heat, ought always invariably to produce, each its appropriated effect, on the power of the cohesive attraction; as water, when its degree of heat is above 32°, is always liquid, so when its sensible heat is below 32°, it should always be solid. But this we know is not always the fact. Water, in some circumstances, can be cooled to 7 or 8 degrees below 32° without being congealed; and many other substan-

ces exhibit the same phenomenon, by retaining their fluidity in some circumstances, after their sensible heat is diminished considerably below their ordinary congealing point. And I now ask, what is the cause which hinders the cohesive attraction from producing its effect, and changing the liquid into a solid? When I find by experience, that, upon disturbing such overcooled liquids, a quantity of heat is extricated from them, which did not appear immediately before, and that, while this heat is extricated, a proportional part of the liquid congeals; I cannot help considering this latent heat which was in it, as having been the cause of its protracted fluidity *."

The same argument, with regard to the cause of fluidity, is repeated by De Luc. "The loss of caloric, which we observe at the moment of liquefaction, proceeds, we are told, from the change of capacity of the substance liquefied. It is not then until the capacity is changed that the heat diminishes; but when the capacity has changed, we have already a liquid instead of a solid. What then is the cause of that change of form? Of this we are told nothing; and it is thus that one of the most important natural phenomena is left unaccounted for †."

Similar reasoning is employed by Seguin, who, to remove the difficulty, and reconcile these opposite opinions, supposes, that the change of form arises from a combination of caloric with the particles of the body suffering it; that then there is an enlargement of capacity; and that the absorption of caloric proceeds partly from the combination into which it enters, and partly from the increased capacity to which he supposes that combination to give rise ‡."

It is to be acknowledged, that there appears a difficulty in the circumstance here pointed out. The temperature of a fluid at its formation, is no higher than that of the solid from

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* Black's Lectures, vol. i. p. 142.

† Idées sur la Meteorologie, tom. i. p. 196.

‡ Annales de Chimie, tom. iii. p. 177. 193.

which it has been formed. By what cause, then, is its fluidity determined; or by what operation can the substance exist, both in the fluid and solid form at the same temperature? Or what can be presumed more probable, than that a part at least, if not the whole of the caloric which becomes latent, produces the change of form, while another portion may be absorbed, from the augmentation of capacity which is the consequence of that change.

The difficulty now stated appears to me to arise entirely from the difficulty of forming a clear conception of the nice balance of antagonist powers, according to the predominance of which the body exists in the solid or fluid state. The fluidity is determined by the operation of sensible caloric counteracting the attraction of cohesion in the solid, until, at a certain point, the attraction is so far weakened as to admit of the particles passing into a new arrangement, and moving easily with regard to each other, by which the fluid state is formed. Let it be granted, that, in a solid body, a force of cohesion is exerted between its particles; let it also be granted, that the operation of caloric is by its expansive energy to weaken that cohesion, according to the quantity of it introduced; from these data, which will not be disputed, it is demonstrable, that there is some point in the thermometrical scale at which, from the operation of sensible caloric, the cohesion will be so far weakened, that the particles will move easily with regard to each other, a state which constitutes fluidity; and that at another point, this remaining cohesion will be completely overcome, and a repulsion established between these particles. Let caloric be communicated to a piece of ice at 20°, its temperature is raised to 25; its particles, by this rise, are so far separated from each other, and its cohesion so far overcome. If more caloric be communicated, the expansion continues to proceed, and the force of cohesion to be weakened. Let 32° be the point at which these two powers are balanced, and at which the body is on the very verge of change, the smallest divisible portion of caloric, a portion by far too minute to be detected by our most delicate instruments, may subvert the balance, and

effect the change. Indeed, ice cannot exist at 32° without melting. At this, therefore, it is past the last point of temperature consistent with solidity, which must be a fractional part below 32°.

This perhaps may be represented more clearly by a very simple diagram. Let the line A B represent the scale of temperature from the zero A to any moderate natural temperature, say 50° of Fahrenheit; and let that part of the line from A to where it is cut by the line C, represent that extent of the scale of temperature in which a body exists in the solid form. If caloric be communicated to the solid through that part of the scale, it will separate its particles, diminish the force of its cohesion, and thus the expansive energy will be always accumulating. It is not difficult to conceive from this representation, that by thus adding caloric, a point will at length be arrived at, in the scale of temperature, at which the antagonist powers shall be exactly balanced, and beyond which, either attraction on the one side, or repulsion on the other, will be exerted. Let the line C intersect A B at this precise point at which the attraction of the solid ceases, so far as to admit of mobility of its parts, it is easy to conceive that this may be an indivisible line, on one side of which the body shall be solid, on the other fluid, and that of course it shall be impossible for us to detect any difference of temperature in the body in the one state or in the other. The same explanation, it is obvious, applies to vaporisation.

I consider this answer fully sufficient; and I regard it not merely as an hypothesis proposed to obviate an objection, but as probably a just representation of the manner in which these changes of form happen.

The violence of the change which Dr Black mentions, is in nowise inconsistent with this view. If the expansion is progressive until it reach a certain point, beyond which it shall be so far weakened as to admit either of a new arrangement of the particles, or of a repulsion being established between them, it is obvious, that in this progression the smallest addition of force,

when the extreme point is arrived at, will be sufficient to produce the most important effect. If a particle be gradually removed, until it is without the sphere of attraction, the moment it is repelled, the repulsion is as strong as at any other distance.

With regard to the fact mentioned in this argument, that water may be cooled 7° or 8° below 32° without returning to the solid state, and the query, "What is the cause which hinders the cohesive attraction from producing its effect, and changing the liquid into a solid?" it is to be remarked, that the introduction of this circumstance merely renders the question unnecessarily complicated; it is a difficulty, properly speaking, with regard to the theory of fluidity, and not peculiarly connected with the absorption of caloric which attends that process; for it is obvious, that it is equally applicable to the one explanation as it is to the other. It may equally be urged against the defenders of Dr Black's doctrine, why, if fluidity depend on a combination of the body with caloric, which combination, in the example of ice, takes place at 32°, and not lower, why is that combination not subverted, when the temperature of the fluid is reduced below this point?

It will even be found more difficult to remove the objection on Dr Black's hypothesis than on the other. In ascribing these changes of form to the prevailing force of one of two opposing powers, cohesion and the expansive energy of caloric, it has already been stated, that this particular phenomenon is explained on the hypothesis, apparently indicated by the phenomena, of a polarity in the particles of the substances in which it is observed; in consequence of which, in becoming solid, they are disposed to pass into certain arrangements, or unite by certain sides in preference to others; that the mere reduction of temperature, at least to a certain extent, does not necessarily place them in those positions in which they are most disposed to unite, but that, by agitation or motion impressed on the particles, some will be placed in these favourable positions, or, by the contact of a solid particle, a surface will be afforded, whence the exertion of the attraction will commence. In this way, this phenomenon

may be explained, independent of any peculiar combination of caloric, while, on the hypothesis of such a combination, it will be found equally difficult to explain, why, when the liquid is reduced in temperature a very little below the point at which it had assumed the liquid state, the peculiar combination on which this is supposed to depend should not be subverted ; or how the subversion of this chemical union should immediately be effected by the contact of a solid particle, or by agitation of the fluid.

In relation to this question, Professor Robison contended *, that fluidity is not to be regarded as arising merely from the separation of the particles of the solid to such distances, that the attraction of cohesion is greatly weakened, but that, in that state, a peculiar arrangement exists among the particles, constituting fluidity ; that there is among them an equality of action, so that, in all positions, they attract each other with the same force ; while, in a solid, there is an inequality of action, or they attract each other more in one direction than in another, whence all positions are not indifferent, and a force is required to change their arrangement. This view of fluidity, I have already observed in the text, is probably just ; but admitting it, it is obvious, that these kinds of action, these dispositions or arrangements, may depend on the distances at which the particles are placed with regard to each other by the powers of cohesion and sensible caloric ; the separation, to a certain distance, diminishing inequality of action, or allowing the polarity to be exerted in a peculiar manner ; and that there is no reason to suppose that such an arrangement in fluids is the result of a peculiar combination of the particles with caloric.

The conversion of a fluid into vapour, is to be explained in precisely the same manner as the fusion of a solid ; sensible caloric producing expansion, and separating the particles from each other. The only difference is, that this proceeds, not only until, as in fluids, the cohesion is much weakened, but until it is entirely overcome, and the particles repel each other ; and there

* Notes to Black's Lectures, vol. i. p. 518.

is a fact with regard to this change,—that it is resisted by pressure, or that, after it has been effected, pressure is sufficient to bring back the vapour to its fluid state, sufficient to prove that this view is just. Pressure, it is evident, can have only a mechanical effect. By resisting the separation of the particles, it may counteract the operation of sensible caloric, and prevent the transition to the aëriform state, or, if applied to a vapour, it may cause an approximation of the particles, and favour the exertion of the cohesive attraction; but we perceive not how it can prevent caloric from entering into a chemical combination, or separate it where it has been combined. The fact is a conclusive one, in proving that the body changes its form first, and that then the caloric is absorbed or disengaged; for the pressure may influence the change of form, by its effects on the distances at which the particles are placed, but cannot obviously influence a chemical combination if it did exist.

There is an absurdity in supposing, that in fluidity and vaporisation it is the portion of caloric which becomes latent that is the cause of the change of form. Fluidity is that state of bodies in which the attraction of cohesion is weak; the aëriform state, that in which it is entirely overcome. Sensible caloric is the power by which cohesion is counteracted. Latent caloric is supposed to be caloric deprived of its elasticity or repelling power, since it produces no expansion, nor any effect on the thermometer. Is it not, therefore, absurd to suppose it capable of producing a change, when this change consists merely in cohesion being diminished or overcome? and must not rather such a change be ascribed to sensible caloric, the agent which is the antagonist to cohesive attraction? In ascribing fluidity and vaporisation to latent caloric, we ascribe them to a cause destitute of those powers necessary to produce them; while it follows necessarily from the powers of sensible caloric, that it is not only capable of producing them, but that there is actually some stage of temperature in every body in which such changes must arise from its operation.

Some have imagined, that the constitution of the gases termed permanent,—their resisting every mean employed to reduce

them to the fluid or solid state, is a proof of the combination of caloric; the attraction of caloric to the bases of these gases being supposed to be so strong, that their change of form cannot be effected; and this is an argument which has been often urged. It is stated with several others not more conclusive, by Professor Robison, in his fifth note to Dr Black's Lectures. This circumstance, however, does not show a more intimate combination of caloric, or a stronger attraction between it and the solid matter. There can be little doubt, but that the difference between the vapours and gases depends entirely on the solid matter of the latter assuming the aërial form at a much lower temperature than the former do; and the analogy between them is so direct and complete, that we may assent with confidence to the doctrine of Lavoisier, that this, and not a more intimate union of caloric, is the sole cause of the apparent difference between them.

The argument which has been stated, in support of caloric being susceptible of exerting chemical affinities, and entering, in consequence of such affinities, into the composition of gases, from the fact that it promotes, or often alone effects, the decomposition of compounds containing an elastic ingredient, is equally fallacious. When an elastic ingredient is combined with a fixed substance, on exposing the compound to heat, it remains undecomposed for a certain extent of temperature; but when this is raised still higher, the decomposition commences: and this has been ascribed to the caloric exerting a more powerful affinity to the elastic ingredient, than the affinity which exists between that ingredient and the fixed one. But it is obviously owing to the mechanical effect, arising from the elasticity communicated by the caloric. There is no proof that any energetic attraction is exerted to the elastic ingredient, or any attraction different from that by which it would be held by this substance as caloric of temperature.

For the reasons I have now stated, it appears to me, that there can be little hesitation in rejecting the opinion, that the absorption of caloric, which accompanies liquefaction and vaporisation, is owing to it entering into a more intimate combina-

tion with the body which has changed its form. If the view now exhibited of these phenomena be just, it is altogether a mistake to make any distinction between what are termed latent and sensible caloric. The fact must no doubt be expressed, that when a body passes from the solid to the fluid, or from the fluid to the aëriform state, a quantity of caloric is absorbed by it, which has no effect in increasing its temperature. But we are not to consider this caloric as existing in the body in a different state from the other portion of caloric it contains; nor is it only at the transition of form that a larger quantity of caloric is necessary to produce in it a given temperature. At every subsequent increase of temperature, the fluid requires more caloric than the solid, and the vapour more than the fluid; and therefore, were such a distinction just, it would require to be said, that at every successive elevation of temperature, a portion of the caloric received by the fluid passed into a latent state.

There can be no doubt but that the caloric, in this state, is combined with the body, or is retained by some attraction; but this attraction is the same as that by which the caloric in a solid body is retained, which modifies the tendency of this power to exist in bodies in quantities proportioned to the space they occupy, which, in a word, gives rise to their specific capacities.

This leads to the discussion, however, whether the difference itself of capacity in bodies, in whatever state they exist, may not proceed from a chemical combination of caloric. By saying that different bodies, or different forms of the same body, have different capacities for caloric, we merely express the general fact, that in equal quantities, and at equal temperatures, they contain unequal quantities of this power. But may this not be owing to a more intimate combination, analogous to chemical union, of part of the caloric,—of that part of it in each body, which amounts to the difference of the quantity it contains, compared with another?

The slightest reflection is sufficient to show that this supposition is inadmissible. If the excess of caloric which one body contains above another, be in a state of combination with it different from that which produces temperature, then the ex-

tity of free caloric, or caloric of temperature, must in all bodies be the same; and, of course, in equal reductions of temperature, they ought to give out equal quantities, proportioned to their quantity of matter. It is only when the body is reduced to the lowest point of the thermometrical scale, that the excess which the one contains above the other, if it were chemically combined, ought to be given out. They give out, however, in all our experiments, unequal quantities; and to account for this, the supposition, that the portion of caloric which one contains above another is in a state of chemical combination, cannot be assigned.

Whether, therefore, the question be considered as relating to the cause, why different bodies contain, at the same temperature, unequal quantities of caloric; or to the cause, why different forms of the same body follow the same law; in neither case, can it be supposed that a chemical combination of part of that caloric, of that part which is in excess, is the cause of the difference; and as the phenomena are in both cases the same, they must be ascribed to the same cause: or, according to the view which I have already given in considering the cause of the different capacities of bodies for caloric, (p. 366-9), that the quantities of caloric in different bodies, and in different forms of the same body, will be in ratios determined by their mechanical structure or the space they occupy, and the specific attraction which each exerts towards it, the whole quantity will be regulated by this law; and there is no reason to believe, that in either case, one portion is in a different state of combination from another. Or, in conformity to Dr Irvine's views, though in language unconnected with any hypothesis, the general fact may be expressed, that caloric, whatever may be its nature, is to be considered as a power diffused over matter; as the cause of that state of bodies termed Temperature; as having a tendency to diffuse itself until a common temperature is formed; but, for the production of this temperature in *different bodies*, and in *different forms of the same body*, unequal quantities of this power are required.

The merits of this theory, contrasted with what is termed

the Doctrine of Latent Heat, cannot be better described than they have been by Mr Leslie. "It was reserved for the celebrated Dr Black to examine the phenomena of the passage to fluidity, with accurate attention; and, had that able chemist discerned all its consequences, or possessed the boldness and ardour of his rivals, he would have deserved our unqualified praise. But he satisfied himself with taking a partial glimpse of the subject; while the theory of *capacity*, at once so luminous and comprehensive, was reared without his participation. Not daring to reject the system of Boerhaave, he sought only to correct it. That correction was however insufficient; for, besides the quantity of heat absorbed in the passage of ice to water, the fluid henceforth requires larger additions than it did in its former state to produce the same ascents of temperature. If the term *latent* expressed merely a simple fact, it might be admitted; but viewed in opposition to its corelative, *sensible*, it conveys an erroneous notion, as if heat lodged in a body consisted of two distinct species or modifications. The ideas associated with the expression *latent heat*, have spread a cloud of mystery and paradox most unfavourable to the progress of real science. Notwithstanding the obstinacy of habit, they are indeed falling into discredit, and must soon melt away into a system which is far more general, consistent and philosophical*."

2d, I have observed in the statement of the subject of this discussion, that there is a different view under which the question, whether any portion of caloric exists in bodies in a state of chemical combination, has been considered. Some eminent chemists, without supposing that the difference in the quantities of caloric in different bodies, or that the absorption of it during liquefaction and vaporisation, is owing to chemical combination, have supposed that there may be a portion of caloric existing in bodies in such a state of combination. This opinion, it is obvious, has no connection with the preceding one, that the caloric absorbed and becoming latent, when bodies change their

* Experimental Inquiry on Heat, p. 532.

form, is chemically combined with them ; and the one may be true, while the other is false.

Lavoisier and La Place inclined to the hypothesis I have now stated, in consequence of their experiments with the calorimeter ; from which it appeared to be proved, that, in different cases of chemical combination, the quantity of caloric rendered sensible does not correspond to the changes of capacity that take place, but is sometimes greater, in other cases less. It appeared, therefore, to follow, that there exists in bodies a quantity of caloric in some other state than what the capacity indicates. This opinion has been still more decidedly maintained by some of the French chemists. They conceive, that, besides the caloric of temperature in a body, the quantity of which is in each regulated by its capacity, there exists another portion chemically combined with the particles of that body, and not productive of temperature.

The principle on which this hypothesis is to be determined, is that just now stated, as regulating the conclusion drawn by Lavoisier and La Place from their experiments. If we find reason to conclude from experiment, that the absolute quantity of caloric contained in a body is precisely proportional to its specific caloric or capacity, it follows, that no portion of caloric in bodies is in a more intimate combination than another ; but if it shall appear, that the absolute caloric, as calculated from experiments, is not exactly as the specific caloric, it is concluded that there will be grounds for drawing the opposite conclusion, and that some portion of that caloric must be in a state of combination.

If it shall be found, by a series of experiments on the changes of capacity from different combinations or changes of form, that the zero is at the same point in the thermometrical scale, it may then be concluded, that the absolute caloric is proportioned to the capacity, and that of course no portion exists in a state of combination ; but if it shall be found, that by calculation from different experiments, the zero is placed at different parts of the scale, the opposite conclusion will be established ; for the determination of the zero depending on the relation

which the diminution or increase of capacity has to the augmentation or reduction of temperature, it follows, that if in some cases augmentations of temperature arise, partly from a diminution of capacity, and partly from a portion of caloric chemically combined being set free, while in other cases they arise solely from diminution of capacity, the zero, as calculated from these alterations of capacity and of temperature, will vary; or if, in all cases, the augmentation of temperature arise partly from the one cause, partly from the other, as there can be no reason for supposing that a constant relation will subsist between these, a variation in the point at which the zero is fixed must be observed. But if the zero turn out uniform, it follows, that caloric is contained in bodies only in proportion to the capacity *.

The experiments which were made by Irvine, Crawford and Gadolin, and which are stated in the section on the absolute quantities of caloric in bodies, were favourable to the conclusion, that the quantity of caloric in bodies is in proportion to their capacities, and that therefore none of it exists in a state of chemical combination. Irvine and Crawford found, in their experiments, that evolutions of caloric were always accompanied with diminutions of capacity in the bodies concerned, and absorptions of caloric with enlargements of capacity, and that these were proportional to each other, or at least the deviations were not inconsistent with that law, or were not greater than might be accounted for from the inaccuracies to which such experiments are unavoidably liable †.

Gadolin instituted a series of experiments with the view of determining this point, by observing the degrees of cold produced during the solution of sea-salt in various proportions in water, and comparing them with those which ought to have been produced from the known capacities of the salt and water, and of the solution after the experiment. The correspondence in these experiments, between the observed and compu-

* Crawford on Heat, p. 377. † Ibid. p. 269.

ted results, is extremely striking, and "put beyond all doubt, that the colds produced are entirely owing to the changes of the comparative heats, and that no part of the heat has been chemically combined." In another series of experiments with sea-salt and snow, the same results were obtained. And in a third, made on the combinations of sulphuric acid and water, any difference between the observed and the calculated capacities, were not greater than what might be supposed to arise from errors committed in ascertaining the former of these, and, from some considerations, it appears must have been owing to that cause *.

The experiments, however, of Lavoisier and La Place, the results of which I have given in the section on the absolute quantities of caloric in bodies, are by no means so favourable to the same conclusion, but appear at first view altogether inconsistent with it; or the absolute quantities of caloric contained in bodies, do not appear to correspond with their specific calorics; and hence the zero, as it is calculated from different combinations, is found at very different points in the thermometrical scale; in one at — 3460; in another at — 7294; in a third — 2630; and in a fourth at a point physically impossible, being $\frac{1889}{-0.01783}$, or 23.8376° of Fahrenheit above 32°.

Does the conclusion then follow from these discordant results, that, besides the caloric contained in bodies proportioned to their capacities, a portion exists in a state of combination, part of which is evolved during their mutual chemical actions?

The admission of such a conclusion rests altogether on the presumption, that, in the experiments in which these discrepancies were observed, the capacities of the bodies concerned, or, what is the same thing, their specific calorics, had been accurately known, this being obviously presumed before it could be decided that these differed from the absolute quantities of caloric; and an error not very considerable in the estimation of

* Crawford on Heat, p. 457.

these capacities would be sufficient to reconcile these discordant results. This is very fairly stated by La Place himself. "The precision," says he, "with which it is necessary to know the specific heats of bodies, renders it very difficult to verify the theory, at least by the combinations which we have employed, owing to this, that the absolute heat of bodies being very considerable, relative to that which they give out in their combinations, a small error with regard to their specific heats will produce a very great error in the absolute quantity of heat." And he adds, "That a very trivial alteration, at most that of a fortieth, in the estimation of the specific heats we employed, would be sufficient to cause all our results to coincide. Now, we cannot say that an error so inconsiderable has not crept into our experiments *."

That it is impossible to ascertain, by the methods hitherto employed, the capacities of bodies with such accuracy as to exclude errors not greater than this, will be admitted by every one who has given any attention to this subject. If those who have bestowed the greatest care on these experiments, and whose accuracy in experimenting cannot be questioned,—Black, Gadolin, and Lavoisier,—have differed in so simple a fact as the quantity of caloric which is absorbed when ice is converted into water, the first stating it at 140 degrees of Fahrenheit, the second at 143°, and the third at 135°, how can it be supposed that we have been able to determine with accuracy the more difficult point, the capacity of a body for caloric? If we examine the table of capacities, we shall find differences in the estimation of the capacity of the same substance, not merely of a fortieth, but of a tenth, or even a fourth. The capacity of alkohol is stated by Crawford 602, by Irvine 930; of sulphuric acid by Crawford 429, by Lavoisier 335; of tin by Crawford 70, by Wilcke 60. Many similar examples might be given; and indeed there are not many instances in which the capacity of a body, determined by two experimenters, coincides so nearly as one-fortieth. It is

* Mém. de l'Acad. des Sciences, 1780, p. 385-6.

evident, therefore, from the admission of La Place himself, that these experiments afford no support to the doctrine of combined caloric.

The same chemists state another experiment, the result of which, in the opinion of La Place, cannot, by the admission of any supposed error, be reconciled with the others. It is that of the solution of nitrate of potassa in water. A degree of cold always attends the solution; and therefore, according to the general theory, the capacity of the solution of the nitrate of potassa must be greater than the mean capacity of the nitre and the water. They give it, however, as less; the calculated capacity being 0.88889, while the real capacity is only 0.8167; and therefore a rise, instead of a fall of temperature, ought to have attended the solution.

The force of this conclusion, however, seems still to rest on the admission of the accuracy of the estimation of the capacities; and it has lately been sufficiently obviated by Dr Irvine *junior*, who by experiment has found the capacity of such a solution of nitrate of potassa to be 914 instead of 816. This agrees, therefore, sufficiently with the result of the experiment. Gadolin had before made the solutions of sea-salt in water, to which La Place likewise refers, the subject of experiment; and had found, that the changes of temperature attending the solution, corresponded very exactly with the changes of capacity.

I must observe, however, that there is another view under which this subject may be considered, more favourable to the doctrine of combined caloric, or which it is more difficult to reconcile with the hypothesis, that the caloric existing in bodies is proportioned to their capacities, or is in no other state than that of free caloric, or caloric of temperature. It is remarked by Berthollet, that the nitrate of potassa, which in the last experiment diminishes the specific caloric of the water, (and even in Irvine's experiment it does so), contains more than 30 in the 100 of oxygen, which retains nearly all the caloric it had in the gaseous form; and, according to Crawford, oxygen gas contains almost five times as much specific caloric as water; whence it follows, that could the absolute caloric in a body be fairly esti-

mated from its specific caloric, the capacity of this salt should much exceed that of water; and of course, the capacity of its solution in that fluid shall also be greater than that of pure water, while it is actually less.

From tracing, indeed, the formation of nitre and some analogous salts, in which much oxygen enters into their composition, without parting with the large quantity of caloric it contains, while at the same time the capacities of these salts are not discovered by experiment to be unusually large, it seems evident, that a quantity of caloric must exist in bodies, which cannot be estimated from their known capacities. To take nitre as an example, and to go no farther back in the steps of its formation than where the evolutions of caloric can be clearly traced, we find, that when the acid which exists in it is formed, by the combination of nitrous gas with oxygen gas, the quantity of caloric disengaged is very inconsiderable, and much less than what is disengaged from the combination of the same quantity of oxygen gas with any other substance; of course much of the large quantity of caloric which oxygen contains must exist in the acid. Again, when this acid is combined with potassa to form the nitre, no great disengagement of caloric takes place; and therefore, this large quantity of caloric, traced from the oxygen into the acid, must also exist in the salt. Yet this salt, it is affirmed, has no great capacity for caloric; and hence it might be concluded, that much of the caloric it obviously does contain, must exist in it in a state of combination more intimate than the quantity contained in it, as indicated by its capacity.

We have some other analogous cases. When ammonia and muriatic acid, each in the state of gas, are combined together, the quantity of caloric extricated is far from being considerable, though in this case two gaseous bodies, by their union, pass into a concrete state; a change of form that might be supposed accompanied with a considerable change of capacity.

On the other hand, if we decompose water by adding to it iron or zinc filings, assisted by the agency of sulphuric acid, a large quantity of hydrogen is rapidly extricated, and passes

into the state of gas. Hydrogen gas has, according to Crawford's estimate, by far the largest capacity for caloric of any known body. We might suppose, therefore, that when a quantity is thus rapidly extricated, it would absorb much caloric, and, of course, that the temperature of the mixture from which it is evolved would be reduced. It does not appear to be so; the temperature being apparently as high as it would be from the mixture of the sulphuric acid and water alone. The case of deflagration affords precisely the same objection.

It may be difficult, perhaps, to give an answer to the objections drawn from these facts, which will be perfectly conclusive; yet there are some considerations which considerably lessen its force.

1st, It is to be remarked, that in all of them the difficulty urged is derived from the supposed capacities of bodies which exist in the aërial form; and when we find so many errors in the determination of the capacities of solids and liquids, which can easily be subjected to experiment, and in quantities so large, as at least to reduce considerably the magnitude of these errors, we cannot suppose that the capacities of aëriform fluids can be determined with much accuracy. Not more than 15 or 20 grains of a gas, says Crawford, can be easily subjected to experiment. To what errors, therefore, must such experiments be liable, when, even in the determination of the capacities of solids, where we can operate on two or three pounds of materials, there are such discordant results? And this, too, independent of other circumstances, which are exclusively sources of error in determining the capacities of aërial bodies. The numbers, which are given on the authority of Crawford, the only chemist who has attempted experiments on this subject, are to be regarded as mere approximations, and, notwithstanding all his attention, it is far from being improbable, are very remote from the real capacities. Hence any conclusion, founded on the supposition that the capacities of the substances are accurately ascertained, or even that they are as accurately given as the assigned capacities of solids or liquids, must be extremely uncertain. The capacities of the constituent parts of

nitric acid may be much less than have been stated; and the capacity of that acid may be such as to retain all that caloric which is not extricated at their combination.

2d, There is another source of error in the reasoning on this subject, founded on a misapprehension of Dr Black's theory of latent heat, which is very frequently fallen into. Because it is demonstrated, that a body in the aëriform state contains more caloric than it does when liquid or solid, it is therefore concluded, that all aëriform bodies must contain more caloric than solids or liquids; and that hence, if, in consequence of chemical action, gases become concrete in a new combination, there should be a copious extrication of caloric; or, on the other hand, when, in consequence of such an action, a gas is evolved from a combination in which it exists, there should be a great absorption of caloric, and a consequent reduction of temperature. The comparison is thus always made between the elements in the gaseous form, and the compound in its concrete state; and from the condensation which the former experience, it is conceived that there ought to be much caloric evolved. Now, this is altogether a mistake. It is true that a body in the aërial form must contain more caloric than the same body in the liquid or solid state; but it is not true that it must contain more caloric, or have a greater capacity than another body which is solid or liquid; and we find even the reverse to be truth. Nitrogen gas has a capacity equal only to 0.793, and therefore much inferior to water, and even to ice; and carbonic acid gas has a capacity exceeding that of water in the proportion only of 1.045 to 1000, and, according to Magellan, inferior to a solution of brown sugar, which he states as 1.086. We perceive, therefore, it does not follow, that caloric should always be evolved in considerable quantity when gases combine and form a dense compound, or that it should be absorbed when a gas is evolved from a dense combination, of which it is an ingredient. Were the capacities of oxygen gas, of nitrogen gas, and of nitric acid, accurately ascertained, it is far from being improbable that the difference in the capacity of the acid from that of its constituents, might be such as would perfectly account for the small evolution of caloric that attends its formation.

Lastly, in all the cases which furnish these objections, there is a source of deception in the quantities of the bodies concerned. When two gases are combined together, and form a concrete substance, we imagine, from the large capacities of the gases, that a large quantity of caloric should be evolved on their union But the quantities of caloric they contain are estimated, not by their volumes, but by their weights; and though the volume of the gases combining may be large, the quantity of matter is really small, and is almost nothing compared with the weight of the vessel in which the experiment must be made. Hence the caloric evolved must be inconsiderable, and this is quickly diffused through the contiguous matter. Thus, in the union of ammonia with muriatic acid, each in the state of gas, the vessel in which it takes place becomes sensibly, but still only moderately warm. Yet, as is justly observed by Dr Higgins with regard to this very experiment, "if a few grains of the gasses can thus heat a vessel of this weight, during the union of their bases, it can be proved, that the liberated caloric was in quantity sufficient to maintain a vaporous state of the salt thus formed, or to make it almost red hot *." In the opposite case of an evolution of caloric, we are deceived in the same way. In the evolution of hydrogen gas, from the decomposition of water by sulphuric acid and iron, we are apt to suppose that there should be a very considerable reduction of temperature, from the large quantity of caloric which the hydrogen gas requires, not recollecting that the weight of the hydrogen evolved is very inconsiderable, compared with that of the materials from which it is disengaged, and that the caloric, the abstraction of which reduces their temperature one degree, may, from this cause, contribute to the elevation of this quantity of hydrogen a number of degrees.

It has been shewn, by actual experiment, that in cases like this, where a gas is evolved in consequence of the chemical action of substances on each other, less caloric is rendered sensible than where the same action happens without the disengagement of

* Minutes of a Society for Philosophical Experiments, p. 80.

the gas. Thus Lavoisier, in an early memoir, proved, that in adding an acid to a pure alkaline solution, a considerable degree of heat is produced from the combination; while, in adding the same acid to the solution of the alkali combined with carbonic acid, there is an actual production of cold; the carbonic acid gas evolved absorbing a large quantity of caloric, which would otherwise have been rendered sensible *.

From these considerations, it must appear, that until we have more accurate methods of ascertaining the capacities of bodies, and the changes of temperature to which alterations in their form or mode of existence give rise, we can draw no strict conclusion from facts such as those that have been stated, against the principle, that caloric is contained in bodies in proportion to their capacities; nor any argument in favour of the hypothesis, that it exists in bodies in a combined state. We never observe, as Dr Irvine *junior* has well remarked, that caloric enters a body without raising its temperature proportional to the quantity that is communicated, unless there be, at the same time, a change of capacity; which change we can ascertain by experiment. Yet why should caloric, if it is capable of entering into intimate combination with bodies, not do so at parts of the scale of temperature at which we can make our experiments, as well as at parts of that scale which are removed from us, and where no direct experiment can be made? Is not this sufficient to convince us, that the supposition, that such combinations take place at these low temperatures, derives any support only from the obscurity in which it is involved? And is it not sufficient also to lead us to regard caloric as existing in bodies only in one state,—that producing temperature, whatever difficulties there may be in estimating, with any accuracy, the quantities, comparative or absolute, which they contain?

The theory of Irvine, which regards caloric as thus existing in bodies in one state, is eminently distinguished by its simplicity, compared with the others. It embraces merely one principle, that caloric is distributed in all bodies, at all temperatures,

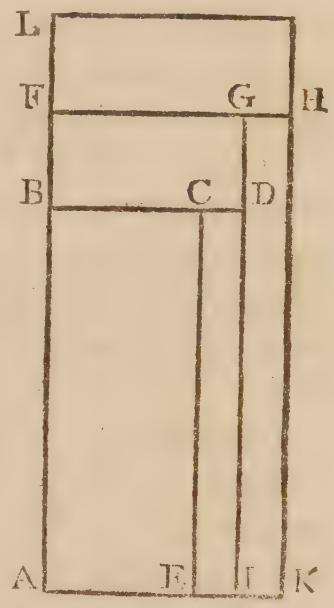
* Mém. de l'Acad. des Sciences, 1777. p. 431.

according to their respective capacities; and that every change of temperature not produced by the direct communication of caloric, arises from a change in the capacities of the bodies, from the mutual action of which, the variation has been produced. Thus, under one principle, established too by experiment as an ultimate fact, all the phenomena of temperature are arranged; while in the other theories, we are embarrassed with the distinctions of latent and sensible, of free and combined caloric,—distinctions as unnecessary as they are hypothetical. It is no doubt true, that the caloric contained in a body, and proportioned to its capacity, may be said to be in a state of combination, or it is retained by an attraction which modifies the law that would otherwise be observed, and by which it would be contained in a quantity proportioned to the volume and temperature. But this attraction is very different from that by which it is supposed the properties of the caloric are entirely suppressed. That such an attraction is exerted, or that caloric exists in any body in a state of combination more intimate than that which produces temperature, is a mere hypothesis, the assumption of which transgresses against that simplicity which is always to be sought for in philosophical investigations, and against the rule which proscribes the multiplying causes to account for phenomena.

Yet this theory, notwithstanding its merit, has not been generally understood, and has certainly not received that consideration to which it is entitled. Though ably explained by Dr Crawford, and applied by him with much ingenuity to the explanation of variations of temperature from chemical action, its justness and importance have not been clearly perceived. Even chemists of the first respectability have scarcely been aware of it, and have employed a language, in explaining the phenomena of temperature, which a knowledge of its principles would have shewn to be incorrect. More attention has lately been paid to the subject, and the theory begins to be regarded in a juster light. "The simplicity," observes Mr Dalton, "of the doctrine of heat maintained by Drs Irvine and Crawford, is to me so strikingly apparent, when contrasted with the now prevail-

ing, but, I think, unfounded distinctions of combined and uncombined or free caloric, that I should be very unwilling to discard it, but upon clear proof of its being incompatible with the phenomena *."

By a very simple diagram, the principal facts relative to the capacities of bodies, the changes they suffer in changes of form, and the determination from these of the real zero, a point so intimately connected with the question regarding combined caloric, may be rendered very obvious, and the preceding reasoning, where it has been obscure, illustrated.



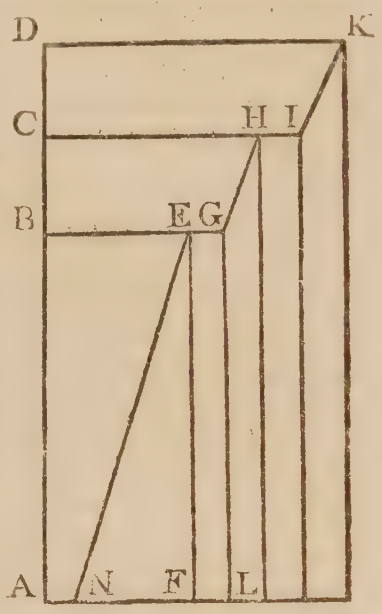
Let the line A B represent the scale of temperature from the real zero A to any existing natural temperature B, and let the line B C denote the capacity of any body at that temperature, the rectangle C A will, on the theory maintained above, that the caloric contained in a body is proportioned to its capacity and temperature, represent the whole quantity of caloric which that body at that temperature contains, and at any inferior temperature this will be represented by the rectangle formed by a line intersecting at right angles the lines A B, E C. Let B be the point at which the body becomes fluid, its capacity is then enlarged, and this enlargement may be represented by prolonging the line B C to D. At the same time, from this augmentation of capacity, a quantity of caloric is absorbed, without producing any rise of temperature. This quantity of caloric, the latent heat of the fluid, is represented by the rectangle D E, the sensible caloric of the fluid at its freezing point by the rectangle C A, and the whole quantity of caloric it contains at that point by the rectangle D A. In

* Nicholson's Journal, vol. v. p. 36.

raising its temperature, quantities of caloric must be communicated to it of course proportioned to its capacity, and these might be represented by lines intersecting at right angles the lines B F, D G, this being continued until it be raised to the point at which it passes to the state of vapour. Suppose this to be at F, the augmentation of capacity which happens when this change takes place, will be represented by prolonging the line F G to H, the quantity of caloric it absorbs from this augmentation by the rectangle H I, and the whole caloric which the vapour contains at the temperature at which it was formed, by the rectangle H A. To represent farther elevations of temperature, the lines A F, K H must be prolonged, and at any point the quantity of caloric contained in the vapour will be represented by the rectangle formed by these, the line A K, and a line intersecting at the part representing that point the prolonged lines A F, K H. By this simple diagram are thus represented, the relation of temperature and capacity, of latent and sensible caloric, the changes in the distribution of caloric accompanying changes of form, and the absolute quantity of caloric which any body at any temperature will contain.

This representation, for the sake of simplicity, has been given, however, on the supposition, that the capacities of bodies are permanent, while it is extremely probable that they are not so, but are progressive with regard to temperature, or become greater as the temperature rises. At the transition of a body to the fluid and aëriform states, the capacity is suddenly enlarged; but, besides this, there is much reason to believe, that in all its forms the capacity is gradually enlarged as the temperature is raised. We know it to be so in the aëriform state; and both from analogy, and from the consideration of what probably is the effect of expansion on capacity, it may be inferred, as I have already stated (p. 381.), that it is likewise the case in the liquid and solid states. On this assumption, and on the supposition that the absolute quantity of caloric in a body is the same as its specific caloric, its relation to this form will be represented by the following modification of the preceding dia-

gram *. The line AD will represent the scale of temperature from the zero A to a certain temperature above that at which the body passes into vapour, C being the point at which it suffers this change, and B the point at which it becomes fluid; the progressive augmentation of capacity which the *solid* suffers in the rise of its temperature from the zero to its melting point, will be represented by the line NE, (A N representing its capacity at zero), and the quantity of caloric which it contains at that point, being still solid, by the rectangle B F. The increase of



capacity which happens at its fusion, will be represented by the line E G, and the whole capacity by the line B G; the quantity of caloric absorbed, by the rectangle G F, and the whole quantity of caloric the fluid contains at the temperature at which it has become fluid, by the rectangle G A. The gradual augmentation of capacity in the *fluid*, as its temperature is raised, will again be represented by the line G H; and the caloric it contains at the temperature at which it passes into vapour, by the rectangle H A. The enlargement of capacity attending that change of form is represented by the line H I; the whole capacity by the line C I; the quantity of caloric absorbed, by the rectangle I L; and the quantity of caloric the vapour contains at the temperature at which it has assumed that form, by the rectangle I A. Lastly, the increase of capacity in the *vapour* as its temperature rises, is represented by the line I K; its capacity at any temperature above its vaporific point

* In this diagram it is assumed, that the augmentations of capacity, as the temperature rises, are regular, except where the changes of form take place, while it is not improbable but that they may be irregular. It is obvious, that any possible irregularity of this kind might be represented, by adapting to it, whatever it may be, the lines N E, G H, I K.

will be represented by a line drawn at right angles from the point denoting that temperature, in the line representing the scale of temperature, until it meets the line I K, prolonged if necessary; as, for example, by the line D K; and the quantity of caloric it contains at that temperature will be expressed by the rectangle thus formed, K A.

In seeking to determine the question as to the place of the zero, and, of course, the question with regard to combined caloric, it has often been supposed, that the assumption of the permanence of capacity at all temperatures, is essential in the calculation. This error is easily committed. By the experiment it may be said, by which we discover the specific calorics or capacities of bodies, we perceive that a given quantity of caloric added to a body, or abstracted from it at a certain temperature, suppose at 32, at 50, or at any of those temperatures at which the experiment can be made, elevates or depresses the temperature of that body a certain number of degrees. By repeating the experiment on another body, or on the same body in a different form, we likewise discover that the same quantity of caloric, measured with accuracy, and communicated to it, or abstracted from it, produces a certain change in its temperature, different from that which the other experienced. We thus discover the relation subsisting between them, in the change which, at these temperatures, they suffer from an equal communication or absorption of caloric. But how do we know, it may be said, that the same relation will subsist between them at all points of the thermometrical scale? It is obvious, that either of them at a temperature, 3, 4, or 500 degrees below the medium temperature of the earth, may experience elevations or depressions of temperature from the communication or abstraction of a quantity of caloric very different from what it would suffer from the same quantity being communicated to it, or abstracted from it at natural temperatures. If in either of them this difference did actually happen, it might be supposed, that from experiments as to the effect on their temperatures from quantities of caloric communicated or abstracted at natural temperatures, we can draw no conclusion whatever as to the relative quantities of

absolute caloric which they contain; and if such differences happened to both, provided the rate of variation was not the same in each, which there is little probability it should, any such conclusion, if drawn, might be very remote from the truth.

This accordingly has often been considered as a just conclusion. "If the capacities," says Seguin, "are not permanent, while bodies do not change their state, the determination of the real zero will always be inaccurate *." And again, "that the capacities should be proportional to the quantities of caloric, it is necessary that they be permanent at all temperatures, while bodies do not change their forms †." Professor Robison has fallen into the same mistake. "Dr Irvine's ingenious method of discovering the temperature of absolute privation," he observes, "evidently presupposes the constancy of specific heat; or, if not constant, it supposes that we know the whole law of variation. Now both of these assumptions are highly improbable. In none of the progressions of natural operations that we are acquainted with do we find this constancy. It is much more analogous to other phenomena, to suppose that, in the temperatures near to that of absolute privation, the quantities of heat necessary for producing equal elevation gradually diminish, and this, perhaps, without end, like the distance of the hyperbola from its assymptote. It is equally probable that the law of diminution may be different in different substances. This will cause the measures of specific heats to change their proportions continually; and therefore the specific capacities observed in temperatures, all of which are far removed from that of the entire absence of heat, give us no means of obtaining the proportions of the accumulated sum of all the heats which has been received into the substances. It follows from this, that even although it should be granted to Dr Irvine, that the heat which emerges, in mixing vitriolic acid and water, or in the freezing of water, is the difference between the absolute heat of the mixture, or the ice, and the absolute heats of the substances before

* Annales de Chimie, tom. v. p. 232.

† Ibid. tom. iii. p. 231.

mixture, or of the water before freezing, still we cannot ascertain those absolute heats, or the temperature of no heat *."

It may be of some importance to show, that this view of the subject is incorrect; and that in reality, in investigating these questions, it is of no importance whatever whether the capacities are permanent or not, or whether we know the rate of their variations, if, as is most probable, they do vary; for, be the variations what they may, excluding the hypothesis of combined caloric, a body at any temperature will always contain caloric, proportional to its capacity at that temperature. This follows as a direct inference from Dr Irvine's experiments; and was shown, though not very distinctly, by Dr Crawford †. It has been since stated more fully and clearly by Dr Irvine *junior* ‡.

This will be apparent, when we consider, that if a body change its capacity, it gives out or absorbs, according as the change is diminution or enlargement, a quantity of caloric proportional to the extent of the change, or to the difference in its capacity before and after that happened. Thus suppose the capacity of a body to be ascertained at 32° of Fahrenheit, and that, in the reduction of its temperature 100 degrees below this, its capacity remains unchanged; in falling each degree, it will give out the same quantity of caloric. Suppose that its capacity is now diminished one-tenth, it will now give out, in falling each degree, one-tenth less caloric than in the preceding period. But then, when the diminution of capacity happened, it would give out a quantity of caloric equal to this deficiency of one-tenth all the way down to the zero; and hence, when it has reached that point, it will have given out, on the whole, just the same quantity of caloric it would have given out, supposing its capacity had remained unaltered. The only difference is, that in that case it would have given it out equally, an equal portion being parted with at all parts of the scale in an equal reduction of temperature, while, in the case we have supposed, it gave it out unequally, or, at the point where the change of

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* Notes to Black's Lectures, vol. i. p. 507.

† Treatise on Heat, p. 10. 56. 451. ‡ Essays on Heat, p. 98.

capacity happened, it parted with a quantity at once proportional to that change, and from that downwards gave out portions in equal reductions of temperature, regular but smaller than it would have done if that change had not taken place. It is obvious too, that supposing the capacity to change a number of times, or suppose it to diminish progressively with uniformity, the results will still be the same; and we may conclude, that, taking the capacity at any temperature, the body will contain caloric according to that capacity, from the real zero to the temperature at which the capacity is estimated.

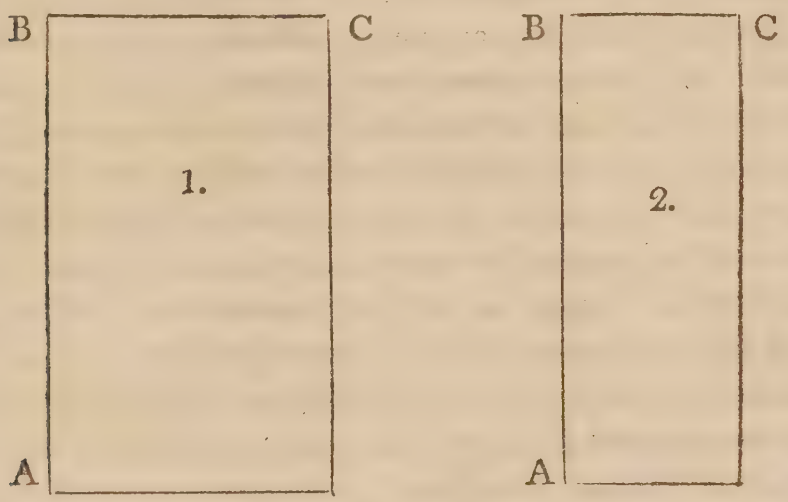
This may easily likewise be illustrated by a reference to the first of the preceding diagrams. Suppose the line A B to represent the scale of temperature from the real zero A to any existing temperature B, and the line B C the capacity of any body at that temperature, the rectangle C A, as has been stated, will represent the whole quantity of caloric which that body at that temperature contains. Let it be supposed, that at the temperature or point B, in the thermometrical scale, which may be assumed to be a low one, or many degrees below any natural temperature, the capacity of the body is enlarged, this enlargement will be represented by prolonging the line B C to D; and if the temperature of the body be now supposed to be raised to the point F, in the thermometrical scale, the rectangle F D will represent the quantity of caloric which it will contain between that point and the point B, where its capacity was enlarged. But it is to be remarked, that when the change of capacity has taken place at B, the body not only requires more caloric to raise its temperature from that point than it did before, but, at the moment of enlargement, it must have absorbed as much caloric as will keep up its temperature, according to its enlarged capacity, from the real zero to the point at which the change happened; and therefore the whole quantity of caloric it contains, at the temperature F, is now represented, not as those would suppose who conceive the permanence of capacity to be a necessary assumption in estimating the absolute quantity, by the united rectangles F D, and C A, but by the rectangle F I. Lastly, suppose that at the point F, its capacity suffers

another enlargement, so as now to be represented by the line F H, it will not only require more caloric to raise its temperature henceforward, but it will absorb, at the moment of change, as much caloric as is requisite to keep up its temperature according to that capacity from zero. At the temperature L, therefore, which we may suppose to be a natural one, or within the reach of our investigation, the quantity of caloric it contains will be represented by the rectangle L K. Now, it is evident, that if from knowing the capacity at the temperature L, we seek to determine the absolute caloric of the body, or at what distance from it the real zero will be found, it is of no consequence, that, at the points F and B in the thermometrical scale, the capacities become less, because at the moment of such an alteration a quantity of caloric will be given out, which, added to what remains, will be equal to what would have been contained, though the capacity had remained unchanged.

It is also sufficiently obvious, that it is quite unimportant whether the changes of capacity be more numerous than those represented in the diagram ; for at each change the same thing will happen which has been already described, or whether they be changes of enlargement or diminution, or, lastly, whether they happen by starts, as represented, or proceed gradually from the zero. The permanence of capacity is therefore not essential in the general proposition with regard to the distribution of caloric in bodies ; but at whatever temperature we found our calculation, *the body will contain a quantity of caloric proportional to its temperature, and its capacity*, proceeding always on the supposition, that no caloric exists in the body chemically combined, or different from that which produces temperature.

I have frequently found, that those not familiar with this subject have experienced some difficulty in conceiving how, since the capacities of bodies are different, and of course the absolute quantities of caloric they contain also different, the real zero should in all of them be the same, or at the same distance from any given temperature. The difficulty arises from it not being clearly understood, that the number of degrees in the thermometrical scale are the same in all, and that the differences in the quan-

tities of caloric they contain arise from different quantities being requisite to raise each of them a degree. Hence, at a given temperature, they are all at the same distance numbered by thermometrical degrees from zero; but in that number of degrees they all contain different quantities of caloric, or, were they to be reduced to the zero, they would in the progress of that reduction give out unequal quantities. In other words, if the zero be supposed to be at 1400 below the freezing point of water, this is to be measured, not by the degrees of any body as a standard, but it is understood that each body at that temperature will contain such a quantity of caloric as raises its own temperature 1400 degrees; though some requiring more, others less, to produce a given augmentation of temperature, they will contain very unequal quantities for the production of that effect. This is very easily shewn by a simple diagram. Let A B (fig. 1.)



represent the thermometrical scale between any temperature, say 32° of Fahrenheit and zero, and B C the capacity of any body, suppose of water, the rectangle C A will represent the quantity of caloric the water contains. Again, let A B (fig. 2.) represent, as before, the scale of temperature, and B C the capacity of another body, say quicksilver, the rectangle C A will again denote the quantity of caloric it contains. It is obvious, that this is much less than in the preceding, though at the same time the distance between the assumed temperature and

the zero is the same. Hence, as mentioned in a note at the bottom of page 417, in estimating the absolute quantity of caloric in a body measured by thermometrical degrees, in other words, the zero or distance from the point of privation, these degrees must always be measured by the capacity of the individual body to which they refer.

Note C.

The opinion that heat and light are essentially the same, or are only modifications of the same substance, has long been maintained. It has arisen obviously from the observation of the intimate connection apparently subsisting between these powers. Light is a common source of heat: it always produces it when in a state of intensity: they are frequently disengaged together, and, when bodies are highly heated, they always become luminous. No better hypothesis, it was conceived, could be proposed to account for these phenomena, than that light and caloric are mutually convertible. Light, in raising the temperature of bodies, was supposed to be converted into heat; and when heated bodies became luminous, the caloric was supposed to be put into a rapid projectile motion, in which state it constituted light.

This theory can scarcely be assigned to any individual philosopher as its author, it has been so long and so generally maintained. Among the modern French chemists, it was in particular embraced and defended by Monge. The same opinion has been adopted by Berthollet in his last publication. Among the British chemists, it was stated with some peculiar illustrations by Dr Higgins, and has been adopted by many others. It has not, however, been implicitly received. Many chemists have considered the question as at least doubtful; while others have maintained that light and caloric are totally distinct.

According to this latter opinion, light and caloric are different kinds of matter. It rests on the principle, that their properties are totally different. Both indeed are capable of assuming projectile motion, but this is not considered sufficient to establish their identity, while their effects on matter are extremely dissimilar. Caloric is diffused over matter slowly and equally, and penetrates every body. It is the cause of expansion, fluidity, and vaporisation. It produces the sensation of heat, but is incapable of exciting illumination. Light is possessed of very different powers: instead of merely raising the temperature of bodies, it produces in them chemical changes, which do not arise from the operation of caloric. If liquid oxymuriatic acid be exposed to heat, the acid gas is expelled from the water without decomposition. If exposed to light, it is decomposed; its oxygen is separated, and muriatic acid remains in the fluid. Nitrous acid is converted into nitric, by raising its temperature moderately. If nitric acid be exposed to light, it is converted into nitrous. Such essential differences in properties, and especially in chemical powers, seem sufficient to authorise the conclusion, that they are totally different kinds of matter.

If the hypothesis, that light and caloric are essentially the same, and differ only in their state with regard to motion, were true, it necessarily follows from the very terms of the hypothesis, that in every thing except what relates to this they should be identical. The assumption is, that they are the same matter, only in different states,—one quiescent, the other moving with velocity; of course, in whatever does not depend on this motion, they must be the same.

This being granted, two principal conclusions follow, and by these we may determine the truth of the hypothesis: 1st, Caloric must be capable of producing precisely the same chemical changes in bodies as light is; and, 2dly, Light must necessarily, when absorbed by bodies, produce heat.

1st, Caloric must, if the hypothesis be true, be capable of producing precisely the same chemical changes in bodies as light. This is so obvious as scarcely to require illustration. The chemical effects of light cannot be supposed to depend on

its mechanical motion : they must arise from the affinities it exerts. In exerting such affinities, or rather in producing the phenomena which arise from them, it enters into combination, of course loses its projectile motion, or becomes quiescent. Quiescent light, according to the hypothesis, is nothing but caloric; and therefore the introduction of caloric into a body should produce the same chemical changes as light. The solar ray, in converting nitric into nitrous acid, or oxymuriatic into muriatic acid, combines with some of their principles. Combined light must, according to this hypothesis, be merely caloric. Caloric directly communicated, ought to be equally susceptible of this combination. Why therefore is it incapable of producing, in these fluids, the same chemical changes? On every hypothesis of their identity, it ought to do so ; while, if they are different kinds of matter, they may be expected to be dissimilar in their effects.

It is incumbent on me, however, to take notice, under this argument, of an explanation given by Count Rumford of the difference in the chemical effects of light and caloric, in conformity with the supposition of their identity *. He observes, that many of the changes which light produces are likewise produced by caloric, when the temperature is raised very high. If the metallic oxides be raised to a red heat, they suffer a partial, or even a complete reduction ; and could we repress the volatility of oxymuriatic or nitric acid, it is not improbable that at such a high temperature either might be decomposed. We know indeed that nitric acid vapour, by being transmitted through a red-hot tube, suffers complete decomposition; and that both acids, when combined with a base by which their volatility is repressed, have their elements separated by such a high temperature. Now Count Rumford observes, that when rays of light strike on a solid body, or on a quantity of fluid, the thermometer affords us no information as to the heat which is exerted at the points on which the rays impinge. It gives us

* Essays, vol. ii. p. 351.

merely the temperature of the whole mass. But it is sufficiently probable, that the points on which they strike may be momentarily heated to a very intense degree, much more than sufficient to occasion decomposition, independent of any chemical agency of light; and in this way the particles of the substance may be successively decomposed. With this explanation, Berthollet, in maintaining the identity of light and caloric, appears to have been satisfied, (Chemical Statics, vol. i. p. 153.).

The hypothesis, though ingenious, cannot be admitted. We have no proof that these decompositions can in any case be effected without the agency of light; for where they are apparently occasioned by the operation of caloric alone, the temperature must always be raised to ignition, when of course light is introduced. But, independent of this, it is at once refuted by the fact, that the rays of light, which are most powerful in producing heat, the red, for example, are the least powerful in occasioning these chemical changes, while the rays which produce them with most rapidity, as the blue and violet, are those which have least heating power. It is obvious, that these facts are altogether inconsistent with the supposition, that the chemical changes which light produces are owing, not to the affinities it exerts, but the heat it excites. Were it true, these chemical changes ought to be produced in greatest intensity by the red ray, since it has the greatest heating power, and even by the invisible calorific rays which do not produce them in any sensible degree; and, on the other hand, the violet ray, which has least heating power, and the invisible rays beyond it which have none, should be incapable of producing these effects, which however they actually do, with much greater rapidity than the others. We must admit, therefore, that the chemical changes produced by light, cannot be owing to the heat it excites, but must be ascribed to the affinities it exerts.

2dly, If light and caloric be the same, differing only in their state with regard to motion, light must necessarily, when absorbed by bodies, produce heat. Here the fact appears at first view to be consistent with the theory, nothing being more familiar than the heating of bodies by the solar rays; and it is

this coincidence which has always been the strongest support of the opinion. The discoveries of Herschel, however, have not only thrown doubt on this supposed fact, but have actually proved it to be false; since they have shewn, that the heating power of the solar rays, is owing to the presence of rays of caloric, or rays not having the properties of light; and that apart from these, the visible rays have no heating power.

Under one point of view, Herschel's discoveries appear favourable to the hypothesis of the identity of light and caloric. We perceive, as it were, in the rays composing the solar beam, the gradations merely of one substance. If we assume the illuminating power as the most characteristic property, we find it placed nearly in the middle of the spectrum, or among the yellow and green rays; it diminishes towards the red ray, and beyond that is lost; though there are still rays in the farther space, possessed at least of some of the properties of light, its subtilty, velocity, reflexibility and refrangibility. It diminishes, too, towards the other side; at the violet it is weak, and beyond that entirely ceases; though still on this side, also, we have rays possessed likewise of some of the properties of light, and having even its chemical powers in a higher degree than the coloured rays. Now it may be said, as Herschel has suggested, that these are ultimately the same kind of matter, and that the rays which are incapable of exciting illumination, are so perhaps from a deficiency or excess of momentum. The rays beyond the red ray, may consist of what may be named Invisible Light; "that is to say, of rays coming from the sun, that have such a momentum as to be unfit for vision. Admitting, as highly probable, that the organs of sight are only adapted to receive impressions from particles of a certain momentum, it explains why the maximum of illumination should be in the middle of the refrangible rays, as those which have greater or less momenta are likely to become equally unfit for impressions of sight." This leads to the conclusions, that all the rays existing in the solar ray are ultimately the same matter in different states; and that since the solar calorific rays have all the properties of caloric, light and caloric are probably the same.

This, however, is only an hypothesis ; and the suppositions involved in it are far from being unexceptionable. We do not find that the calorific rays are capable of exciting illumination by condensation, as we ought to expect, were the hypothesis just : on the contrary, Herschel found the reverse when they were condensed either by a mirror or lens. And a very striking experiment made by Ritter, seems sufficient to subvert it, —that of combining the two species of invisible rays, those beyond the violet, and those beyond the red, without producing any visible light. This he did, by transmitting by two lenses each species of rays, so as to bring the space beyond the violet ray of the one spectrum, and that beyond the red ray of the other to correspond ; but from this intermixture of rays, no illumination was obtained : the power of the chemical rays appeared to predominate. It is obvious, that were the visible rays a medium between the invisible calorific and the invisible chemical rays, some species of visible light ought to have been produced in this experiment. Besides, how are the decrease on the one side, of the chemical power of light, while its heating power increases, and, on the other side, the increase of the chemical, with the decrease of the heating power, to be explained ? An increase of momentum might increase both, or a diminution of it diminish both ; but on no hypothesis that these rays are gradations of the same common matter, possessed equally of the heating and the chemical power, can it be explained how the one should be diminished as the other is augmented.

But there is likewise another point of view, as I have remarked, under which these facts fall to be considered, which affords a refutation of the hypothesis of the identity of light and caloric. The principal foundation of it has been, the production of heat from the solar rays. It seemed difficult to explain how this happened, but from the conversion of light into caloric. In the hypothesis under discussion, it is a necessary consequence that light should always produce heat when its motion is stopped, or it is absorbed ; for being supposed to be merely caloric in rapid projectile motion, when it passes from

that state it must act as caloric, and raise the temperature of bodies. We have seen, however, that from the experiments of Herschel it results, that light has actually no heating power; that, therefore, when stopped or absorbed by bodies, it is not converted into caloric, the heating power of the solar rays being owing to a very different cause. It is unnecessary to recapitulate the proofs of this, which are fully stated in the text, (page 521.). The fact is established, and it subverts the very foundation of the opinion, that light and caloric are the same.

The phenomena of phosphorescence are still more unfavourable to this hypothesis, and prove the total inconvertibility of light by quiescence into heat. It is assumed in the hypothesis, that light, when quiescent, becomes heat. By exposing a phosphorescent body to light, a portion appears to be absorbed; of course, retained by the body, it becomes quiescent; it may be disengaged as caloric, but should not again become light, unless the body be put into such a state from entering into chemical combination, or from some other cause, as to enable it to project particles of caloric with the velocity of light; and in this case no necessary relation should appear between the previous exposure to light and its subsequent emission. The phenomena of phosphorescence are, however, altogether different. If a phosphorescent body be exposed to light, and then removed to a dark situation, it will retain this light, continue to emit it slowly, and at the end of some weeks be still luminous. Surely were light merely caloric, in a state of projectile motion, the light must have been converted into caloric, and could not be emanated in this form. If it be said the emanation arises merely from a property of the body itself, in consequence of which it puts into the state of projectile motion this matter of heat and light, it is obvious, in this case, that its shining should be independent of previous exposure to light. The facts, that it requires that exposure; that after it, it will continue to shine, but only for a limited time; that the light emitted gradually diminishes, and at length ceases;—these prove, that light has been imbibed; that it has been retained for a length of time in the body, and is then emitted;

facts which must at once shew, that light, by quiescence, is not converted into caloric.

From these facts, there appears little reason to doubt of the falsity of the hypothesis, that light and caloric are the same matter in different states of motion; since the two general suppositions which it necessarily involves, that light in quiescence should become caloric, and that light should always have a heating power, are false. No other assuming the identity of these agents has been proposed worthy of notice. The vague proposition, that they are modifications of one common principle, cannot be adopted as a philosophical theory: if their identity be assumed, some explanation must be given of their apparently different properties; and if none be advanced, the proposition itself is not entitled to claim any discussion.

On the principle that light and caloric are totally different, all the phenomena arising from the action of these powers may be explained. The greater number of them indeed shew dissimilarity of action, as has been already pointed out, and of course are not only explained on that principle, but are proofs of its truth. It is only necessary, therefore, to give an explanation of those phenomena, which appeared to prove similarity of action, and which were regarded as proofs of their identity.

With regard to the production of heat by the action of light, there can now be no difficulty. In every case in which it happens, we can discover the presence of invisible calorific rays, and it is to their action that the production of heat is to be ascribed. From the laws, too, which we know radiant caloric to observe, the phenomena attending the production of heat by the sun's beams, such as that it is greatest in black bodies, least in those of a white colour, greater in those which are rough and spongy than in those the surface of which is smooth, are equally well explained; for precisely the same differences are to be observed in the heating of bodies by radiant caloric alone. There is therefore no reason from these phenomena to admit the hypothesis of the convertibility of light into caloric.

There is as little for the supposition that caloric can be con-

verted into light. When the temperature of a body is raised sufficiently high, light begins to be emitted, and its emission continues as long as the temperature is kept up. This forms the state of ignition, or incandescence. On the supposition that light and caloric are different, whence is the light derived, and by what cause is it rendered sensible?

It might be supposed, perhaps, that the light emitted is merely that contained in the body, and which is expelled by the repulsive agency of caloric. What is unfavourable to this supposition is, that a body can be kept in a state of ignition by preserving its temperature sufficiently high for any length of time. Were the light it emits that which it previously contained, it must necessarily be in limited quantity. Did the illumination, therefore, depend on it, it must become gradually fainter, and at length cease. Yet when we consider the extreme subtilty of light, perhaps this objection has no force. It has been determined with considerable probability, that the quantity of light emanated from the sun, cannot be greater than one-forty thousandth part of a grain from a square foot of surface in a second of time. We perceive, too, that the very minute quantity of light which can be absorbed by a phosphorescent body, in exposure for a minute to the solar rays, is sufficient to render it luminous for many days. If, therefore, the high temperature of ignition weaken the affinity of light to bodies, we can easily perceive, merely from this subtilty of light, that it may continue luminous for a long, almost an indefinite time, while that temperature is kept up.

It may also be remarked, however, that the light in ignition may be derived from the same source as the caloric is supplied from. If we put an incombustible body among burning fuel, it soon becomes incandescent; in this state its temperature is raised to an equality with that of the burning matter; and it projects copiously rays of radiant caloric. Whence is this caloric derived? It is obviously a portion of that which is rendered sensible by the combustion of the fuel, with which the incandescent body is penetrated, and which it emits. It is also projecting rays of light: Whence is this light derived? The

same source is obviously to be assigned. It is a portion of that light which, as well as caloric, is evolved by the combustion of the fuel, and which, like that caloric, penetrates the incandescent body, and is projected from its surface. In every case of ignition, excited by communication, it will be found, that the light emitted by the incandescent body may be derived from the matter, by communication with which that state is produced, and is ultimately, as well as the caloric, evolved from chemical combination. It can be retained in that matter for some time; but if withdrawn from the source of supply, the emission, both of light and caloric, becomes less, and that of light very soon entirely ceases.

I must observe, however, that there is one experiment which appears unfavourable to this explanation, and which has been regarded as subversive of any explanation of this kind. It is the experiment of Mr Wedgewood already described, (p. 256.), in which air was found not to be luminous, even when its temperature was equal or superior to ignition, though in this state it could render a solid body to which it was applied luminous. Here, therefore, apparently a body is brought to the state of ignition, merely by the contact of heated matter, without light being at the same time conveyed to it. It is sufficiently probable, that by this arrangement the state of ignition might be indefinitely kept up; and therefore the light evolved cannot be supposed to be merely the light which the body contains, disengaged by the high temperature. How then is the result of this experiment to be explained otherwise than by supposing caloric to be convertible into light? *Caloric* alone appears to be supplied by the air; yet *light* is given out by the body suspended in it. It is accordingly stated by Berthollet, as proving the identity of light and caloric *.

I believe no explanation has been given of this interesting fact; yet it appears to me to admit of one which is satisfactory, on the theory that light and caloric are different, and not convertible. The force of the argument depends entirely on

* Chemical Statics, vol. i. p. 421.

the supposition, that light could not be conveyed by the air, without that air being luminous; a supposition, I conceive, to be false. Illumination is excited only when a certain number of rays come from a body to the eye; and if the number be diminished, though many rays may still be emitted, the illumination is not perceived. We have sufficient proof of this in phosphorescent bodies. They are luminous for some time after exposure to the sun, but they gradually become dark; yet still when they fail in exciting the sensation of illumination, they are emitting rays of light, as we can prove by rendering the organ of vision more sensible by preparation. If a person remain in the dark for a considerable time, he will be able to perceive illumination in many of those bodies, in which otherwise it could not be discovered, as Beccaria and Wilson have amply shewn. We find the same to hold true with regard to ignition itself. An ignited body will be easily discovered by shining in the dark, while in day-light it is perfectly obscure. To what is this owing, but that the rays it emits are too few to excite the sense of illumination, when the eye is stimulated by rays of light from every object around it?

I can easily conceive, then, that every particle of an aëriform fluid may be actually in a state of ignition; yet it shall not, from its minuteness, be visible; and the whole mass shall not appear luminous, merely from its tenuity, or the small number of minute particles that come within the sphere of vision. To excite that sensation, it is clear, that a certain number of rays from a given point are necessary. If a cubic inch of air contain a number of solid, but very minute particles, not equal to the 1000dth part of what are contained in a cubic inch of a solid or liquid, it is obvious, that the latter may excite illumination, while the other will not, though the individual particles of each are emitting rays of light of the same intensity. But if a current of air in this state be directed on a solid body, the common law of ignition will be observed; the ignited particles applied to the solid will at length render it incandescent, and preserve it so while the current is sufficiently kept up, and that solid, from its density, will appear luminous.

In reality, what renders an aëriform fluid invisible? If it consist of solid particles, placed at certain distances, these particles must reflect the rays of light which fall on them; and we know that solar light, in passing through the atmosphere, suffers considerable diminution. This reflected light must reach the eye; but there not being a sufficient number of rays from a given point to excite vision, the particles are not perceived. And such may be their minuteness and distance, that they may even reflect or emit much more light without being perceptible, or without illumination.

From these facts, no doubt, I conceive, can be entertained, that in the experiment of Wedgewood light might, and even must have been conveyed by the air to the solid body, though that air was not itself luminous.

The production of ignition by friction or percussion, may be stated as an example in which there is not the same supply of light from an external source, and which, therefore, cannot be explained on the principles now stated. I have already remarked at the end of the article on ignition, that it is not proved that this species of ignition can be kept up for an indefinite time; and the light evolved, is probably the light contained in the body, and separated by the high temperature which the friction or percussion excites. From the extreme subtilty of this principle, as I have already remarked, little difficulty can be attached to the supposition, that if the state of the body be unfavourable to the affinity by which light is retained in it, that light may continue to be extricated for almost an indefinite time. Besides, on the supposition that the light emitted in ignition arises from the caloric assuming that form, the difficulty is only removed one step back; for how is this caloric supplied? If we can admit of an unlimited source of caloric in the body, we may admit of a similar source of light; or if the subject is supposed to be so much involved in obscurity, as, with regard to the one, to admit of no satisfactory explanation, the same shield of obscurity may be thrown over the other.

From the fact that light and caloric are often evolved together, it has been conceived that an intimate connection subsists

between them. By the common cause by which the evolution is occasioned, it is conceived that part of the principle of which they are modifications is put into projectile motion, part more slowly emanated, whence it appears under the form both of heat and light. Accordingly, it has been stated, that where a combination evolving caloric proceeds rapidly, part of that caloric is evolved as light; where it takes place slowly, heat only is produced; the degree of light being, "*cæteris paribus*, proportionate to the velocity with which the caloric is emitted," and there being no illumination "from bodies which, during their combination, emit the caloric either slowly, or in circumstances in which manifest impediments prevent the projection of it with the velocity necessary to the constitution of light *."

It is no doubt true, that where light and caloric are evolved from a combination, the more rapidly it is performed, the quantities will appear greater, because more are extricated in a given time; but that the rapidity of combination does not determine the evolution of light, or cause caloric to appear under that form, is obvious from a very slight review of chemical phenomena. What combination is more rapid, and attended with greater condensation, than that of nitrous gas and oxygen gas, or muriatic acid gas and ammonia, and yet no light is evolved, though there is no obstacle from the density of the product, or any other cause, to prevent the caloric from assuming, if it were capable of it, the projectile state, which is supposed to constitute light? Or, on the other hand, what combination proceeds more slowly than the spontaneous combustion of phosphorus in atmospheric air, where the quantity of light emitted, if we consider the time, must be considerable? In the example of nitrous gas, more oxygen is combined in a minute, than in that of phosphorus in several days, though during that time the phosphorus is always luminous, at least in the dark.

Some facts have also been stated to shew, that, according to the density of the medium, a combination may evolve either

* Minutes of a Society for Philosophical Experiments, p. 303.

caloric alone, or caloric and light. Dr Higgins gave the example of the oxygenation of pyrophorus, or of phosphorus in nitric acid, where heat only is produced; while, in its oxygenation in the vapour above, which must consist partly of nitrous acid vapour, and partly of nitrous gas, the oxygenation is attended with light. Whatever may be the cause of this difference, (and it is to be remarked that the agent oxidating the phosphorus is in these experiments *not* the same, and the products of its decomposition are different,) the cause assigned cannot be admitted; for we know that in many cases of chemical action not more rapid than this is, a dense medium is no obstacle to the emission of light, as in the burning of phosphorus under water by the medium of oxymuriate of potassa and an acid, and still more is this conspicuous in phosphorescent bodies, the feeble light of which is not restrained by immersion in a fluid.

On the hypothesis, that light and caloric are different principles, the evolution of the one, in cases of chemical action, has no necessary connection with that of the other. The evolution of caloric is owing to a change of capacity, and the quantity will be greater or less as that change is greater. If one or both of the substances combining contain light as a constituent part, and if the compound they form have not an attraction to it, an extrication of it will also attend the combination. But this has no necessary relation to the heat produced; and if the bodies combining do not contain light as a constituent principle, or if the compound they form has a sufficient attraction for it, there will be the evolution of caloric without that of light, as in the combinations of many gases with each other, nitrous gas with oxygen, or ammonia with the acid gases, in the absorption of gases by water, and in the mutual action of many substances in the liquid or solid form.

We have accordingly, from chemical union, heat without light, heat with small quantities of light, and light with comparatively inconsiderable evolutions of caloric, and these in all varieties of rapidity of combination, and accompanying condensation. Where the quantity of caloric evolved is considerable,

there is generally an extrication of light, apparently owing to the cause which the phenomena of phosphorescence fully establish, that a high temperature weakens the affinities of bodies to light. The occasional disengagement, therefore, of light with caloric in chemical action, and its constant disengagement when the temperature is raised very high, afford no proof of the identity of these principles, since they are equally explained on the opposite hypothesis; and even on the supposition of their identity, no cause can be assigned, why the caloric should at one time be evolved in part under the form of light, at another time not, and why no proportion, regulated by the circumstances of the combination, can be discovered in the quantities evolved under each form.

These are all the arguments that have been advanced in support of the hypothesis, that light and caloric are ultimately the same principle, that are worthy of any notice. Their insufficiency is apparent; and though there may be some obscurity with regard to the relations between these agents, as there is indeed in every thing regarding their nature, we may, in the present state of our knowledge, consider them as essentially distinct.

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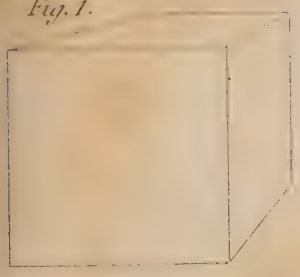

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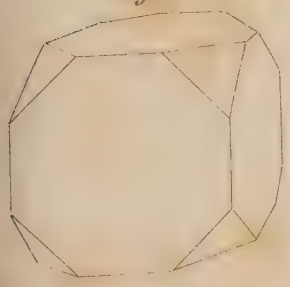

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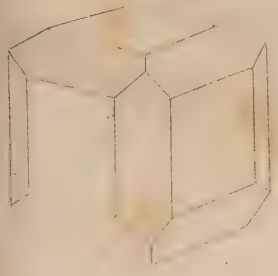

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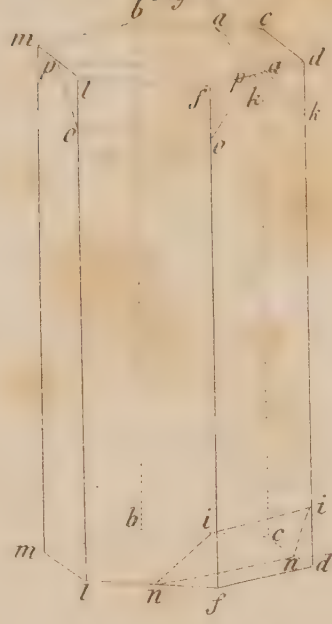

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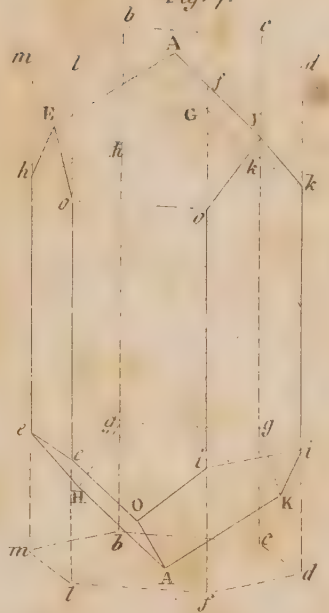

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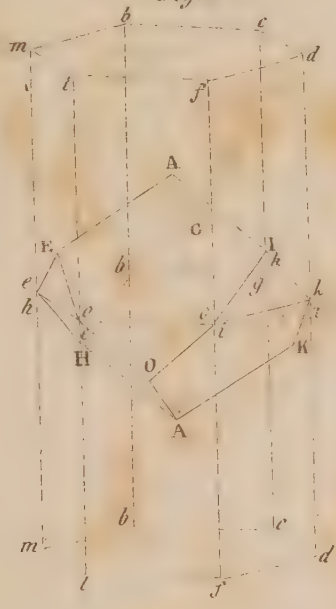

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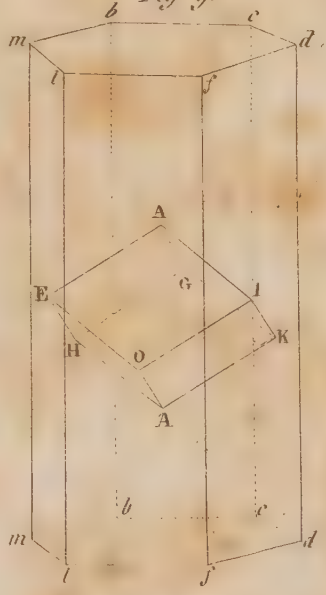

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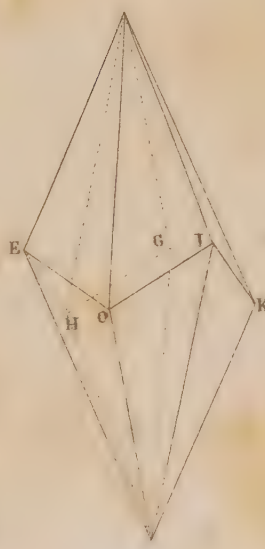

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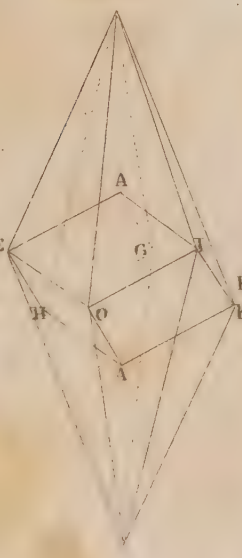

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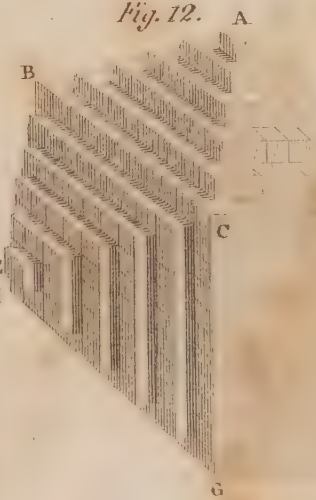

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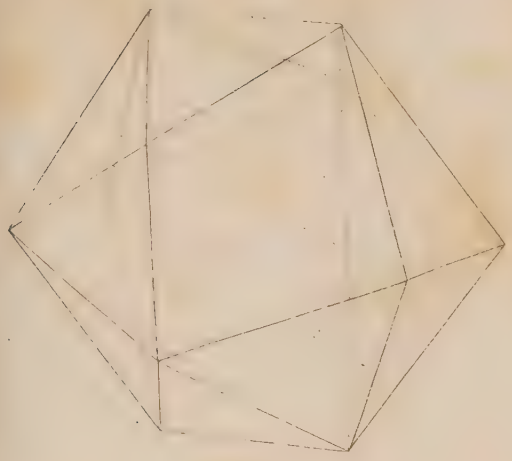

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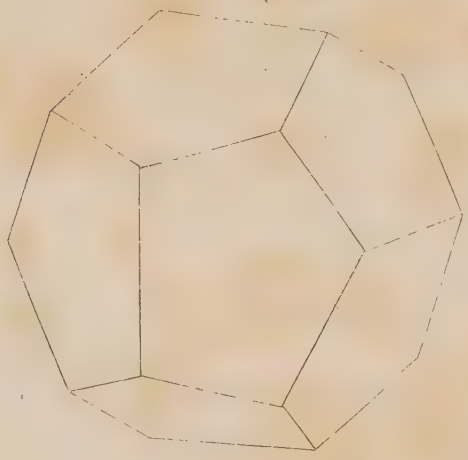

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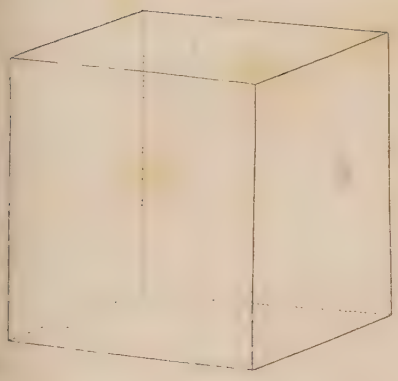

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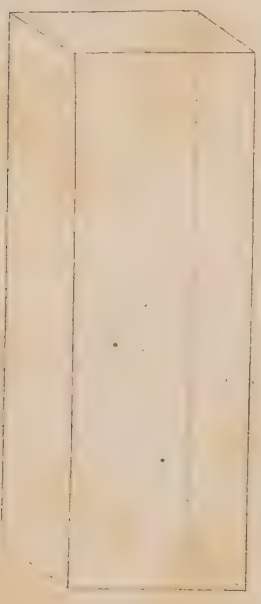

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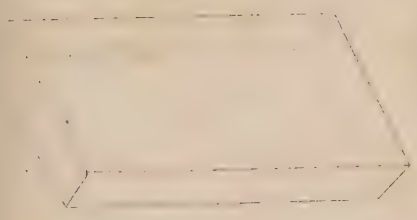

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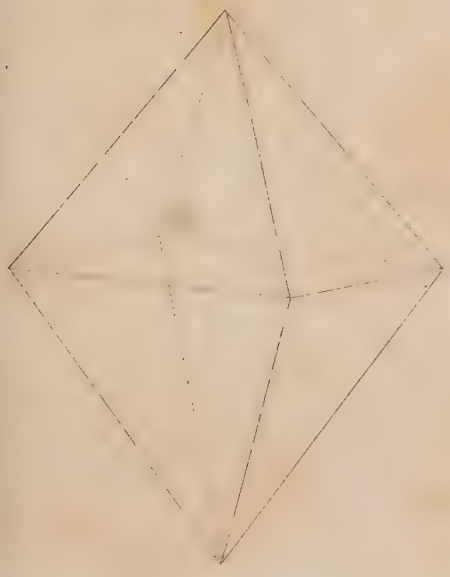

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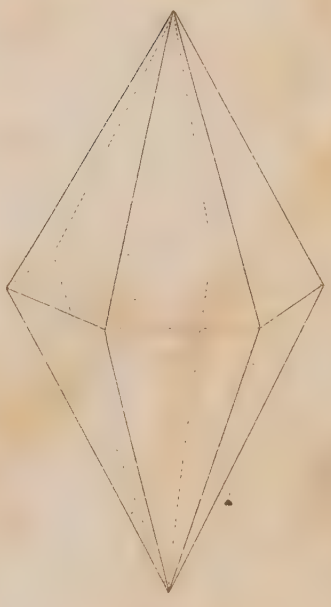

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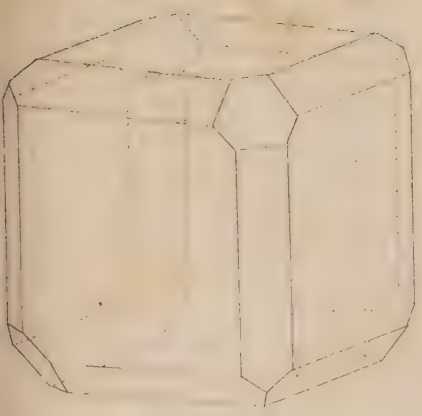

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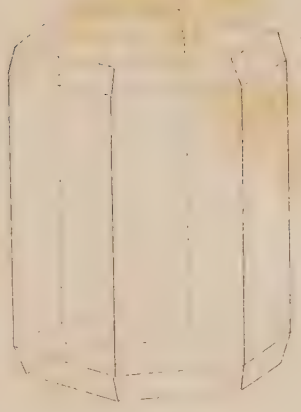

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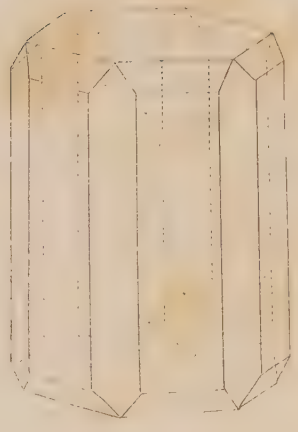

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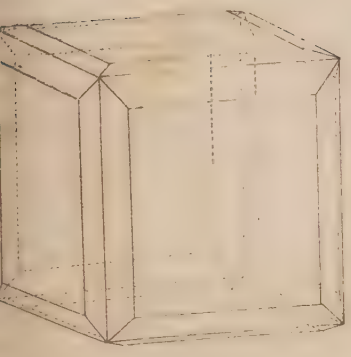

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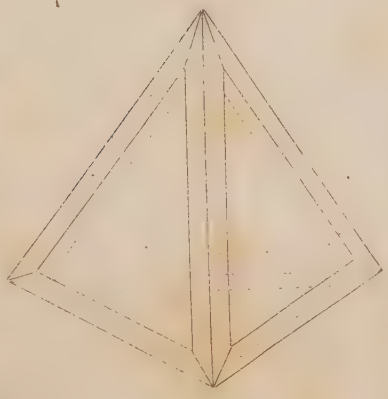

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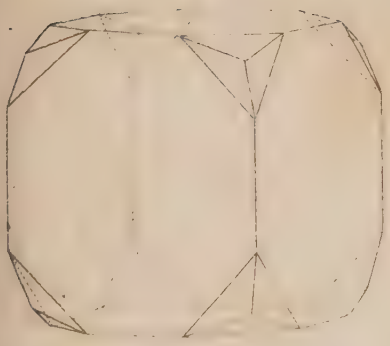

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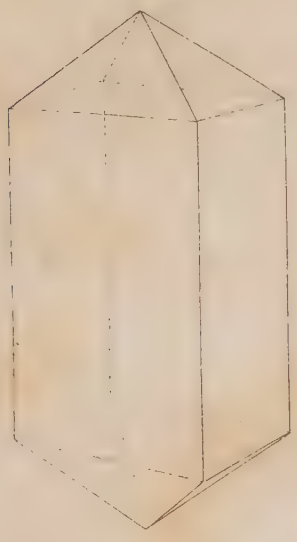

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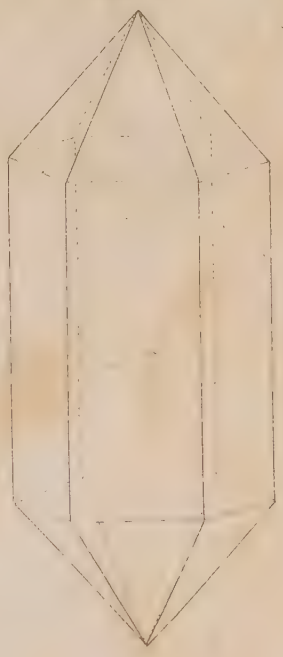

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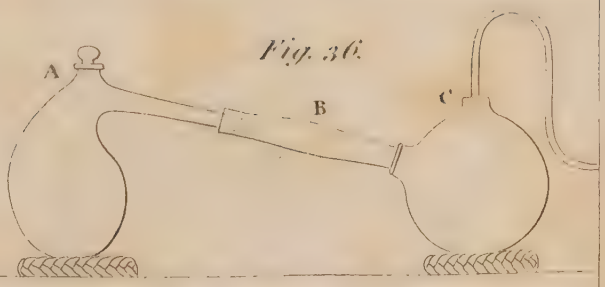

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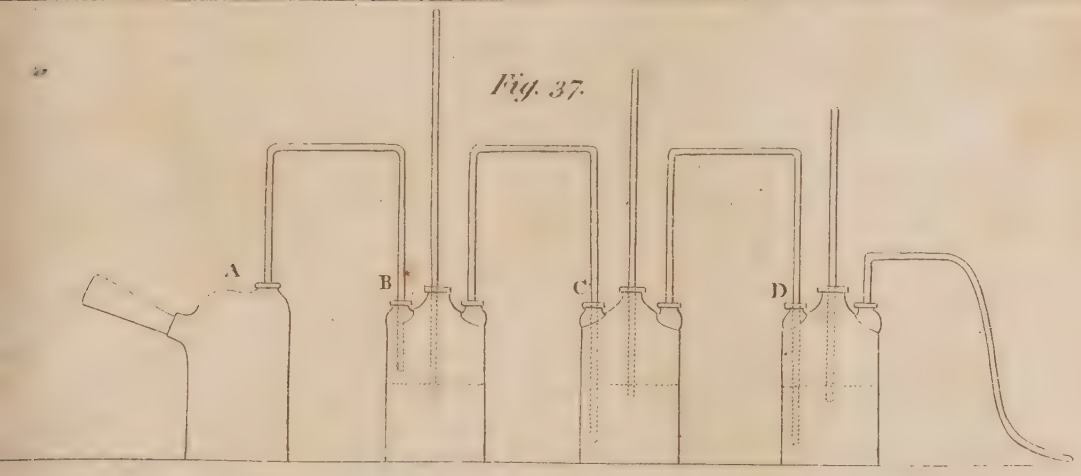

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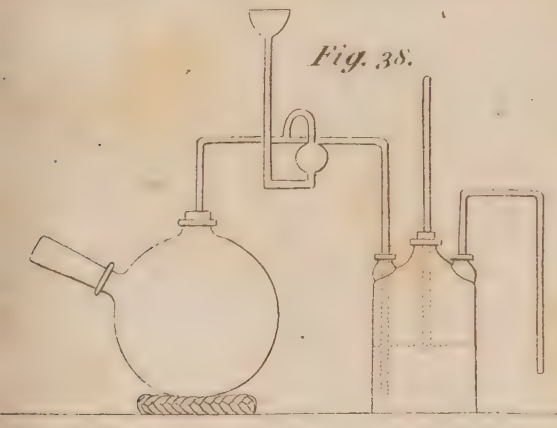

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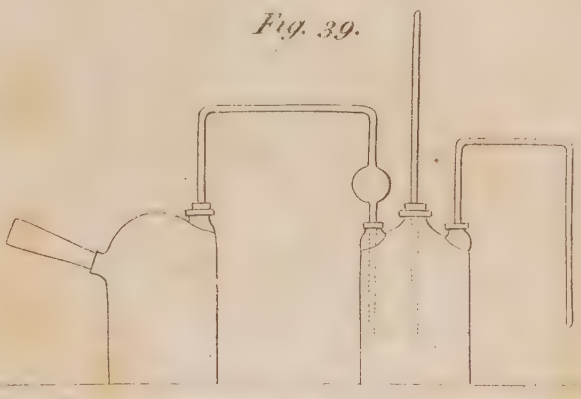

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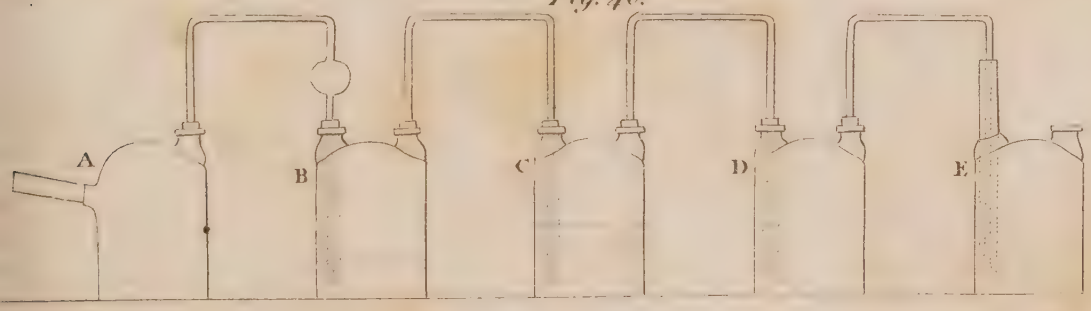

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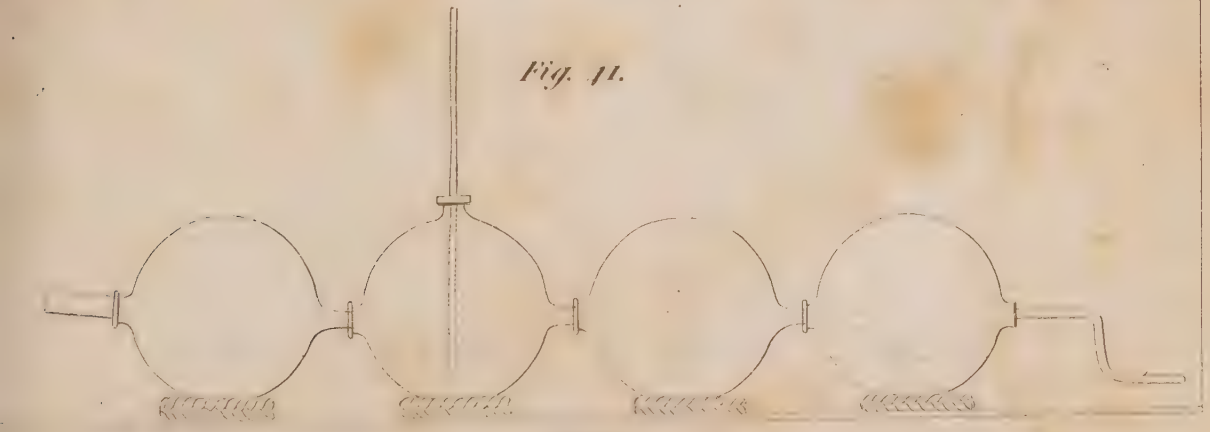

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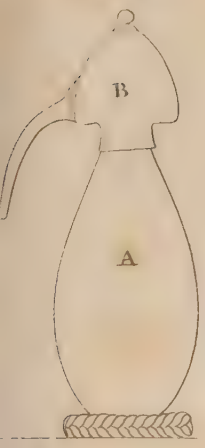

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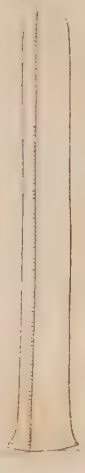

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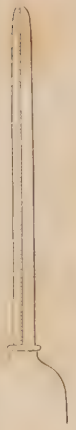

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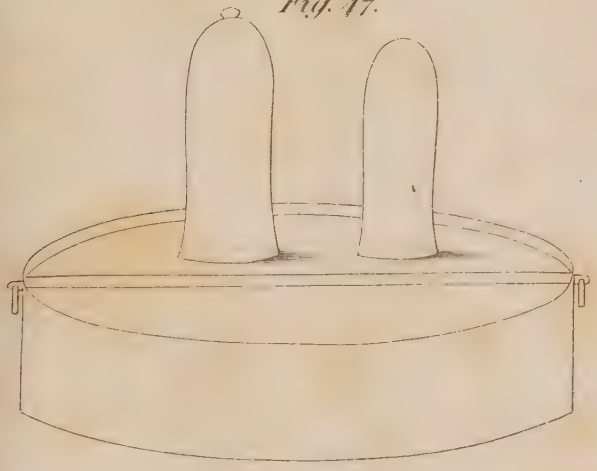
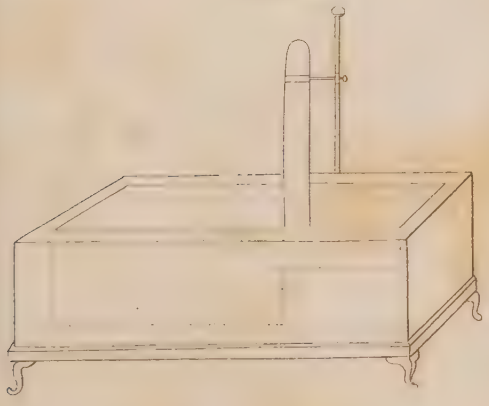


Fig. 18.



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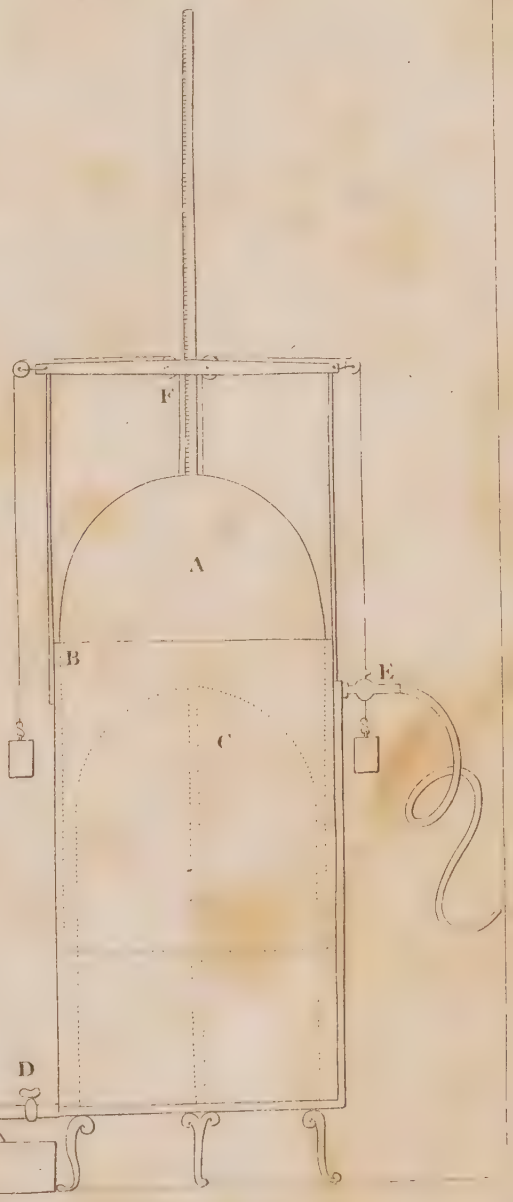

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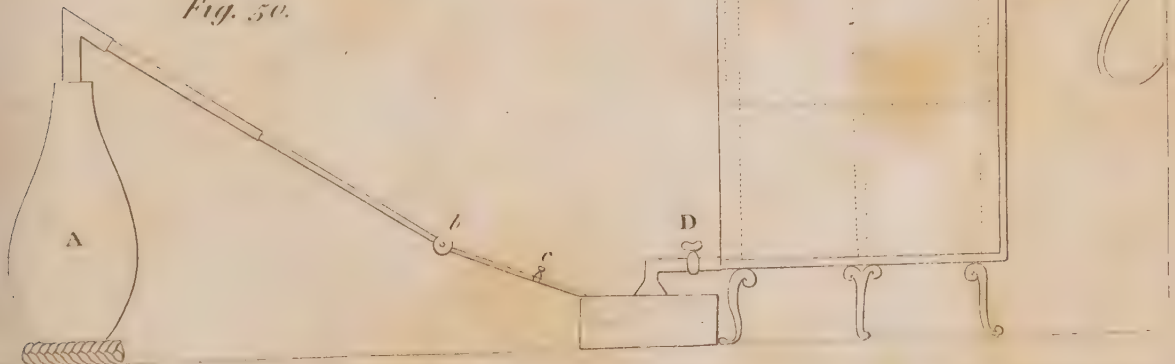
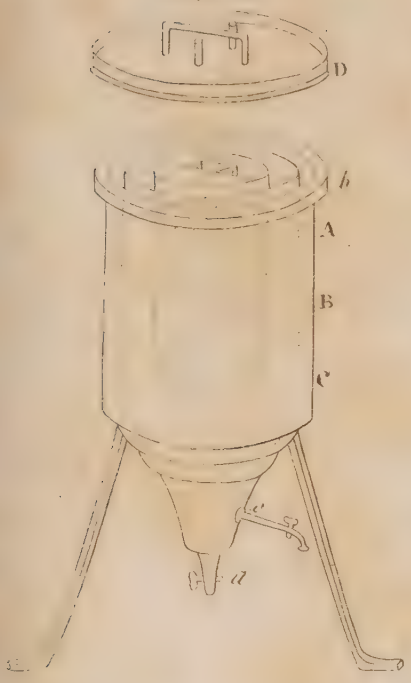


Fig. 51.



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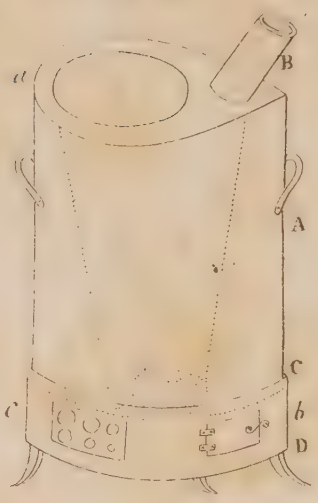

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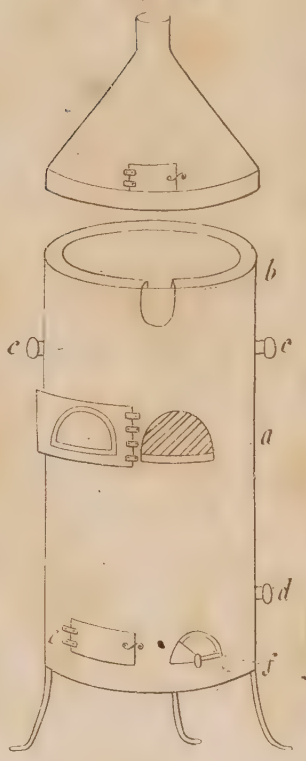

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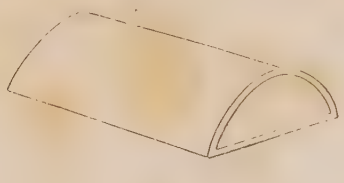

Fig. 55.

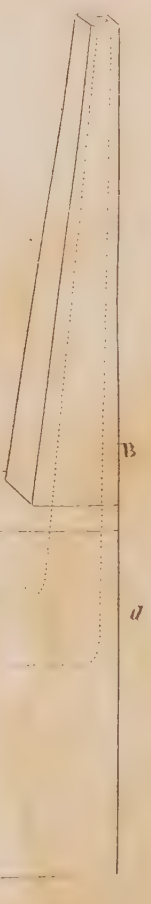

Fig. 54.

Fig. 56.

Fig. 57.

Fig. 58.

Fig. 59.

Fig. 60.

Fig. 61.

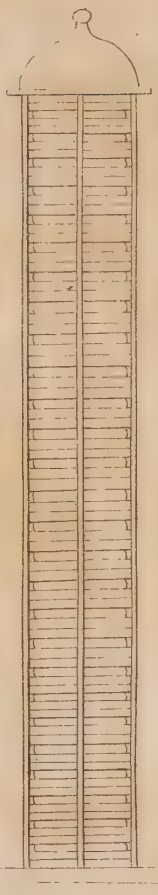

Fig. 63.

Fig. 62.

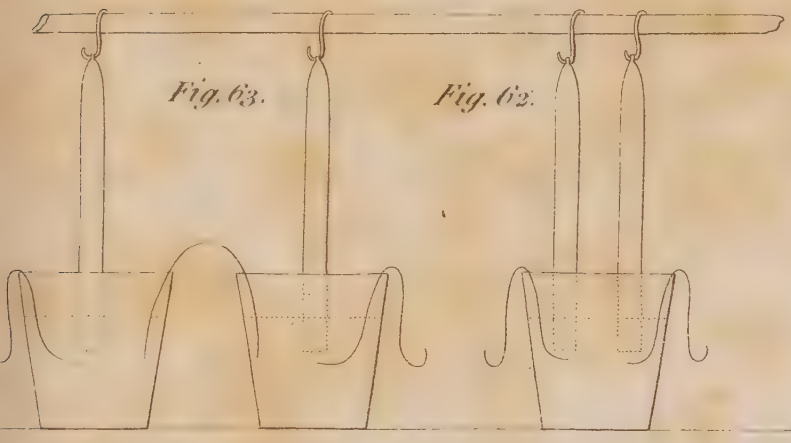

Fig. 64.

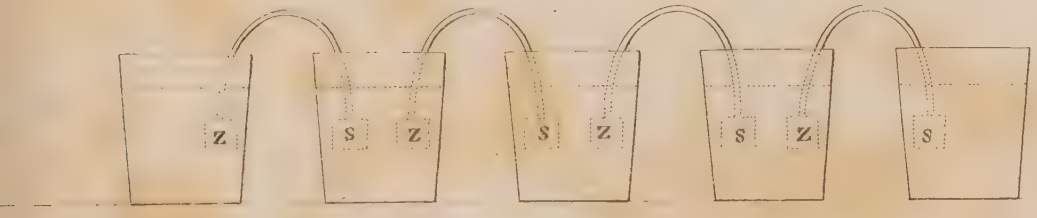

Fig. 65.